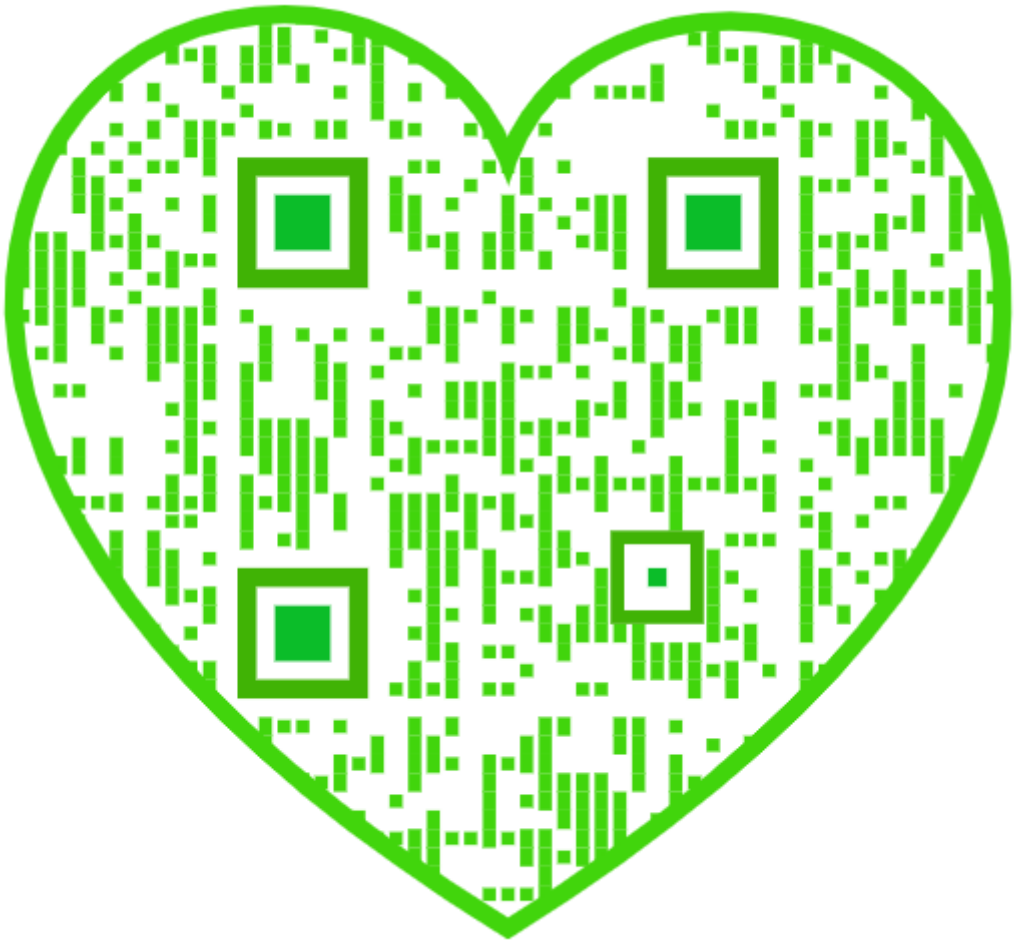

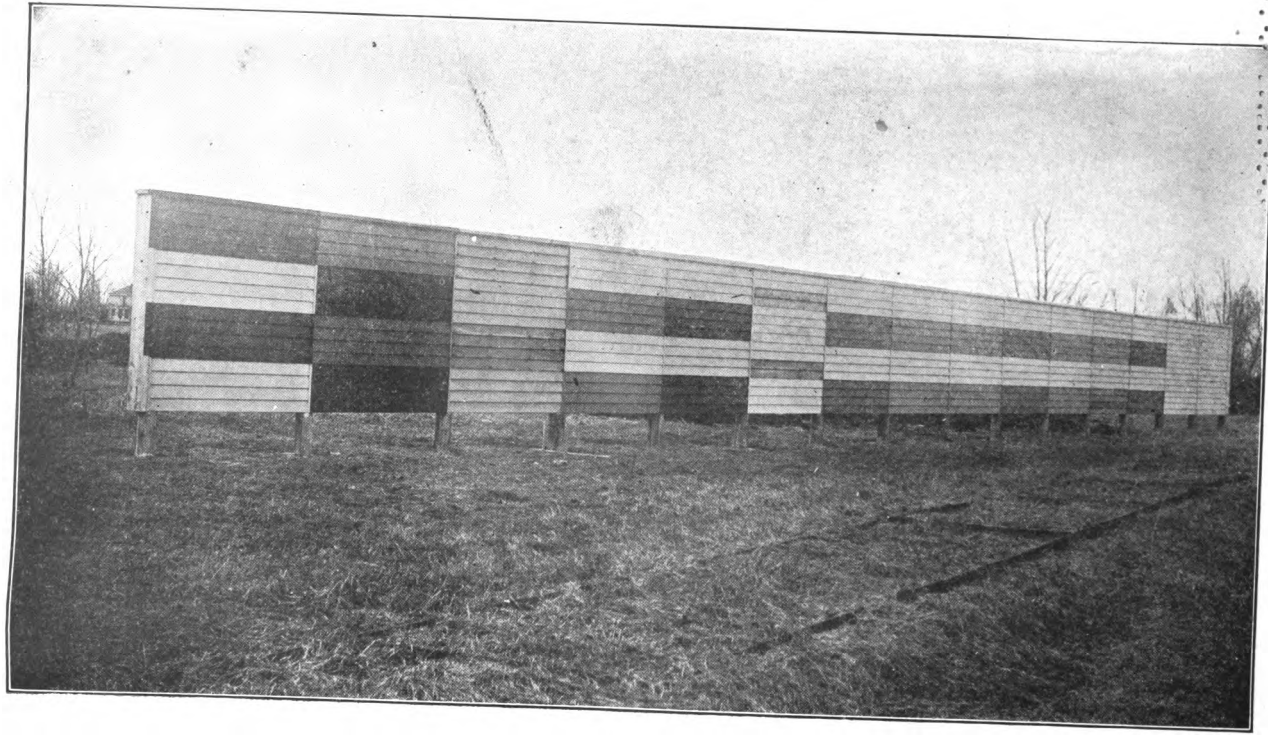

Frontispiece

ANALYSIS OF PAINT AND VARNISH PRODUCTS

BY

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CHIEF CHEMIST ACME WHITE LEAD AND COLOR WORKS

FIRST EDITION

FIRST THOUSAND

UNIV. OF CALIFORNIA

NEW YORK

JOHN WILEY & SONS

LONDON: CHAPMAN & HALL, LIMITED

1912

TP 935
H59

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Stanbope Press
F. H. GILSON COMPANY
BOSTON, U.S.A.

PREFACE.

AN extended experience in the mixed paint industry and in the manufacture of white lead and other lead products has convinced the author that there is need of a more comprehensive work on the analysis and valuation of paint products than has hitherto appeared.

The enactment of various laws regulating the sale of prepared paints and the discussions arising therefrom have done much to stimulate chemical analysis and research work with the various paint products. New combinations have been brought to the attention of the consumer, who must rely on the chemist, official or private, for their valuation and suitability for use. The rapid development of the industry and the increasing sharpness of competition has placed an added responsibility upon the paint chemist of to-day; his methods must not only be accurate, but must also be capable of securing results with the greatest possible rapidity.

It has been the endeavor of the author to present in this volume such methods as he has found accurate and at the same time rapid and convenient. A considerable number of the methods are substantially the same as those given in his earlier work, "Analysis of Mixed Paints, Color Pigments, and Varnishes." The scope of the work has, however, been greatly enlarged, a large number of new methods have been introduced, with many new paint products, whose properties are discussed, while a large amount of data relative to the

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composition of the various paint specialties to be found on the market, has been included.

The author wishes to express his appreciation for the assistance given him by his many friends in the preparation of this work.

CLIFFORD D. HOLLEY

DETROIT, MICHIGAN,
April 12, 1911.

CONTENTS

		Page
Introductory Chapter.	The Proper Labeling of Paint Products	1
Chap.		
I.	Separation of Vehicle from Pigment	4
II.	Estimation of Water in Paints	11
III.	Water Emulsions and Emulsifiers	17
IV.	Estimation of Linseed Oil and Its Adulteration in Mixed Paints	23
V.	Determination of the Purity of Linseed Oil	32
VI.	Determination of the Purity of Linseed Oil (*Continued*)	42
VII.	Analysis of the Volatile Oils	51
VIII.	Turpentine Thinners	59
IX.	Turpentine Substitutes	72
X.	The Inert Pigments	77
XI.	Analysis of White Lead	92
XII.	Analysis of Sublimed White Lead and the Zinc Pigments	104
XIII.	Analysis of Sublimed White Lead and the Zinc Pigments (*Continued*)	116
XIV.	Determination of Fineness, Covering Power and Tinting Strength of Pigments	124
XV.	The Practical Testing Out of Paints	129
XVI.	Analysis of White Paints	143
XVII.	Analysis of White Paints (*Continued*)	153
XVIII.	Kalsomine, Cold Water Paints and Flat Wall Finishes	163
XIX.	Composition of Colored Paints	170

Chap.		Page
XX.	Analysis of Indian Reds, Venetian Reds, Tuscan Reds, Red Oxides and Ochres	175
XXI.	Analysis of Black Pigments and Paints	185
XXII.	Analysis of Brown Pigments and Paints	196
XXIII.	Analysis of Blue Pigments and Paints	204
XXIV.	Analysis of Yellow, Orange and Red Chrome Leads, Analysis of Vermilions	211
XXV.	Analysis of Red Lead, Orange Mineral and Litharge	221
XXVI.	Analysis of Paints for Manufacturing Purposes	227
XXVII.	Composition and Analysis of Fillers	233
XXVIII.	Shingle Stains, Barn and Roof Paints	236
XXIX.	Analysis of Japans and Driers	239
XXX.	Analysis of Shellac and Spirit Varnishes	245
XXXI.	Analysis of Oil Varnishes	257
XXXII.	The Practical Testing of Varnishes	269
XXXIII.	Varnish Stains and Color Varnishes	279
XXXIV.	Enamels and Varnish Specialties	282

UNIV. OF CALIFORNIA

ANALYSIS OF PAINT AND VARNISH PRODUCTS

INTRODUCTORY CHAPTER.

THE PROPER LABELING OF PAINT PRODUCTS.

1. **Let the label tell the truth.** It is indeed unfortunate that large quantities of ready-mixed and paste paints are sold to-day more on the strength of the vigorous advertising conducted by the manufacturers than on the merit of the products themselves. The extravagant claims of the manufacturers and the many instances of detected fraud have aroused the consumer to the need of adequate protection. To this end numerous state paint laws have been enacted requiring the composition of each paint product of whatever description to be printed on the label. This procedure has been met with vigorous opposition on the part of the paint manufacturers, who claim that they are thus compelled to reveal valuable trade secrets. Such, however, is not the case, as in no instance has it been found necessary to place on the label, in order to comply with the various laws, any information but that which a competent chemist could ascertain with ease.

2. **Fraud confined to certain classes of paints.** A careful examination of the situation will show that fraud and abuse have been confined almost without exception to white leads so called, paste paints, and ready-mixed house and barn paints; in other words, to

paint products in which *varnish* is not an essential constituent. The various paint specialties, such as carriage paints, enamel paints for various purposes, etc., are of such a nature that the manufacturer cannot afford to take chances in exploiting an inferior article, and he must manufacture, if he desires to be successful, as good a product as he can for the price for which he sells it.

It therefore seems unwise to surround with rigid regulations a class of products with which no fraud has been practiced and which is not readily susceptible to fraudulent practice. It is only reasonable to believe that the lawmakers desired to regulate the sale of such paint products as they were acquainted with and which are the more common ones in everyday use; and to require labeling as to composition of paints containing varnish as an essential constituent is going a step beyond the possibility of practical enforcement and at the same time is not justified by present conditions.

3. **Necessity for labeling mixed paints.** The practice of labeling a low-priced mixture of barytes, whiting, and zinc oxide as *strictly pure white lead* and claiming a high degree of wear and durability for a mixed paint containing considerable quantities of water, a large excess of benzine, and a high percentage of extenders like barytes, clay, whiting, etc., will not cease until the sale of such products is regulated by law and the purchaser is given ample opportunity of knowing just what he is buying. Such combinations may have a commercial value, but the selling price should be determined accordingly, and chemical analysis can be depended upon to show their probable service value.

Valuation of paints by analysis. It is indeed probable that chemical analysis alone will not enable the pur-

chaser to select the best wearing paint from among several, if each is composed of white lead and zinc oxide, with possibly a small percentage of inert pigments, suitably ground in pure linseed oil, and a requisite amount of turpentine drier added, even if the percentage of the different constituents vary considerably.

In such instances, however, the analysis will indicate that the purchaser is at least securing a fair product for his money, and if properly applied may be depended upon to give satisfactory service. Also, if he possesses even a moderate knowledge of the value of paint ingredients, the placing of the analysis on the can will enable him to select a paint the composition of which is most nearly in accord with his ideas.

4. Placing an additional burden on the manufacturer. Requiring all paint products to be labeled as to composition places an undue burden of expense upon the manufacturer, which is by no means slight, owing to the immense variety of his products, each of which is likely to appear in several shades or colors. On the other hand, requiring him to place the analysis on paints, whether ready-mixed or in paste form, in which varnish is not a necessary ingredient, involves a slight cost only, and at the same time efficiently protects the consumer.

CHAPTER I.

SEPARATION OF VEHICLE FROM PIGMENT.

5. Preparation of sample. If a dry color, and in bulk, great care must be exercised in securing a uniform sample, which should be thoroughly mixed on the mixing cloth. If the sample be a liquid paint in the unbroken package, the brand, manufacturer, and guarantee, or other statements of importance appearing on the label, should be carefully recorded. The can should also be examined for any evidence of leakage, or any markings indicating the date of manufacture. On opening the package the unfilled portion should be measured by placing a straightedge across the top of the can and measuring with a ruler the distance downward to the surface of the oil. The gross weight of the package should also be recorded at this time.

6. Condition of sample. The clear oil portion should be carefully removed with the aid of a pipette or suction flask, and the surface of the paste portion remaining should be examined carefully for evidence of any precipitation of the drier constituents, which will often form a gummy layer on the surface of the paste. The older the sample the more pronounced the precipitation. The condition of the paste portion is readily ascertained with a steel spatula, and the degree of settling, hardening, and any separation of the coarser particles due to poor grinding, should be noted.

7. Obtaining a uniform sample. The paste is then completely removed to a larger can, known as the mixing can, which should be kept solely for this purpose,

and stirred until smooth. The reserved oil portion is gradually added, with constant stirring, which should be continued until the analyst is thoroughly convinced that the sample is uniform in composition. The entire success of the analysis depends upon securing a uniform sample, and more analyses are incorrect because of carelessness in the preparation of the sample to be analyzed than from any other source.

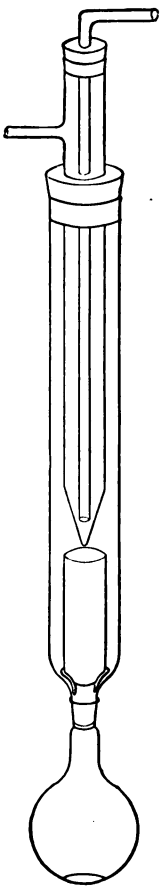

FIG. 2. EXTRACTION APPARATUS.

8. Weight. The weight of the cleaned can subtracted from the gross weight gives the net weight of the sample. The can is then filled to the height occupied by the sample, as noted above, with water from a carefully graduated measure, thus giving the net volume of the paint. The can is then filled to the brim with a measured amount of water and the capacity of the can recorded.

9. Separation of the vehicle. Much difficulty is often experienced in extracting the vehicle from the pigment, due to the fineness of the pigment particles and the ease with which they pass through the walls of the extraction tubes. This difficulty, however, may be avoided by the use of the apparatus illustrated below. The extraction thimble, containing a filter folded cylindrically, is dried in the hot-water oven for thirty minutes, weighed, and 10 to 15 grams of the sample weighed into it, extracted with ether for 24 to 36 hours, dried, and weighed again. The loss in weight represents the

vehicle, and the residue remaining, the pigment, which is reduced to a fine powder and kept tightly stoppered until examined. Any casein or similar product in the paint will remain unextracted by the ether and unless detected will interfere with the proper analysis of the pigment. With very finely divided pigments like Prussian blue a thickly padded Gooch crucible may be used; the successive extractions may be decanted into it, using a strong suction and refilling the Gooch before it sucks dry.

10. **Extraction with acetone.** If the paint contains a considerable percentage of water the extraction can be best accomplished with the use of a good grade of acetone. Many chemists prefer a solvent prepared by mixing 50 parts benzol, 30 parts wood alcohol, and 20 parts refined acetone.

11. **Removal of vehicle in quantity.** Another method of obtaining sufficient vehicle from a paint for the determination of the volatile oils, the quality of the linseed oil, etc., is to fill a tall cylinder with such of the sample as is not needed for the water estimation (100 to 150 grams) and for obtaining the free pigment, corking it tightly, and placing it in a tall copper can filled with water heated to about 70° C. By reducing the viscosity of the oil in this manner the pigment will settle quite rapidly, and in 24 hours, if the temperature is maintained at 70° C., sufficient oil may be siphoned off with the aid of the suction pump.

12. **Use of centrifuge.** By far the most convenient method of obtaining sufficient vehicle for examination is by centrifuging the paint. In the average laboratory an electric centrifuge is the most convenient type. The cylinders used may be of glass, but preferably of aluminum, as the pressure on the ends is often severe

when the centrifuge is in motion. The bottoms of the cylinders should be removable, being screwed onto the cylinder. This permits of the easy removal of the precipitated paint and the rapid cleaning of the cylinders.

13. **Balancing the cylinders.** It is necessary that the cylinders opposite one another be evenly balanced, and it is always advisable to balance up the cylinders on the scales before placing them in the centrifuge. The cylinders should be tightly corked to prevent loss by evaporation of the volatile thinners, and live steam admitted into the centrifuge chamber sufficient to heat the contents of the tubes to about 70° C. In the majority of cases the pigment will be thrown out rapidly and cleanly and, by using a number of cylinders, an ample amount of the oils may be easily obtained.

14. **Power centrifuges.** In the factory laboratory, where steam pressure is always available, an ordinary Babcock butter-fat test can be conveniently used, the steam leakage into the upper chamber being sufficient to keep the tubes warm enough to insure the rapid precipitation of the pigment. The machine selected for this purpose should be very strongly made. One of the safest and most satisfactory centrifuges on the market is that illustrated in this connection (Fig. 3), manufactured by the International Instrument Company, Cambridge, Mass.

15. CENTRIFUGAL FORCE IN CENTRIFUGES.

Centrifuge Head.	Capacity of Tubes in c.c.	Average Rotating Diameter in cm.	Force in Lbs. per Lb. in Revolutions per Minute.						
			600	1200	1800	2400	3000	3600	4000
8-place combination	500	43	86	344	774	1380	2150	....	....
	250	40	80	320	720	1280	2000	....	....
	100	44	88	352	792	1480	2200	....	....
	50	38	76	304	684	1216	1900	2740	....

EXAMPLE: A cup, weighing 2 pounds, at a speed of 3000 r.p.m., would exert a stress of 4000 lbs. on its trunnions.

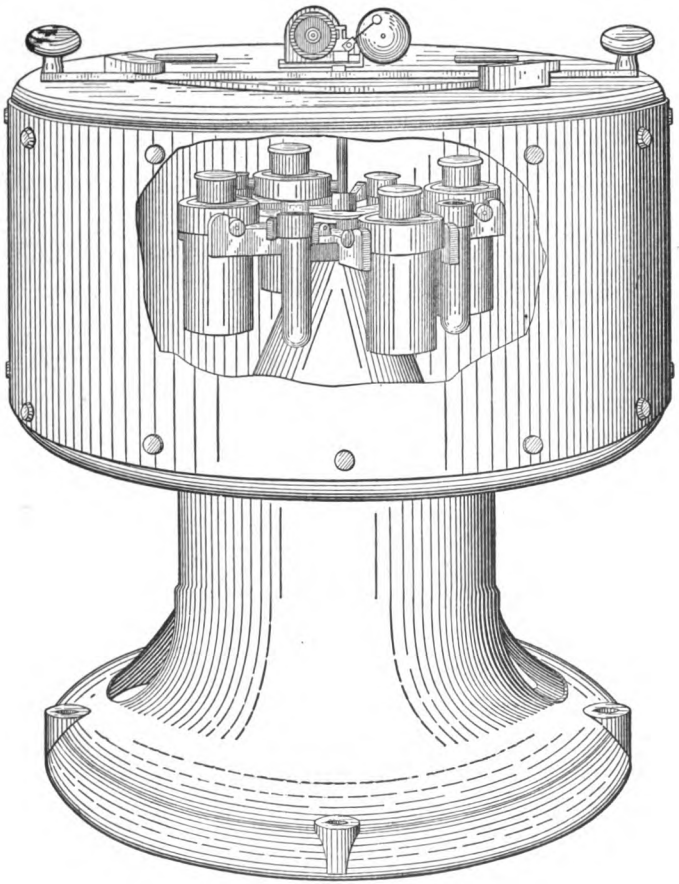

FIG. 3.

16. Cushioning of glassware. A rubber cushion should be supplied for each tube. Place a little water in the metal tube, insert the glass tube, press down, and allow the water to overflow the metal tube. If

this care is taken in the matter of balancing pressures and of cushioning there should be very little breakage of glassware.

17. Rapid separation of pigment. If only the pigment is desired the separated oil may be poured off and the precipitated pigment stirred up with benzine, centrifuged, and the operation repeated once more. This will insure the removal of practically all the linseed oil, only a trace remaining. When dried the pigment should receive an especially careful mixing, as the centrifuging causes the pigments to settle to a certain extent according to their specific gravities.

18. Typical analyses[1] of white and gray paints from the same manufacturers, showing the change in the ratio of pigment to vehicle:

	I.		II.		III.	
	White.	Lead Color.	White.	Gray.	White.	Gray.
Pigment	65.6	57.2	62.6	54.9	63.2	54.9
Vehicle	34.4	42.8	37.4	45.1	36.8	45.1
	100.0	100.0	100.0	100.0	100.0	100.0
Vehicle:						
Linseed oil	88.9	89.5	86.0	84.7	97.0	83.9
Drier	9.3	8.6	12.6	13.8	2.0	14.9
Water	1.8	1.9	1.4	1.5	1.0	1.2
	100.0	100.0	100.0	100.0	100.0	100.0
Pigment:						
White lead	14.65	14.18	44.08	27.29	50.52	33.98
Lead sulphate	0.34	0.27	4.62	4.39	.00	2.84
Zinc oxide	63.42	63.27	41.41	50.94	46.06	41.80
Calcium carbonate	.....	.....	4.59	7.10	3.18	6.94
Silicia	20.91	20.14	.....	.....	.....	12.14
Magnesium silicate	.....	.....	5.10	6.94	.....	.....
Undetermined	0.68	2.14	0.20	3.34	0.24	2.30
	100.0	100.0	100.0	100.0	100.0	100.0

[1] Analyses by the author.

19. Ratio of pigment to vehicle. It is customary with a large number of manufacturers to have one ratio of pigment to vehicle for white paints and another ratio for the tints. In some cases this is necessary, owing to the low specific gravity of the tinting colors, but in many instances where only one or two per cent of color is added to the white base it is not necessary materially to reduce the proportion of pigment.

CHAPTER II.

ESTIMATION OF WATER IN PAINTS.

20. Occurrence. A fraction of 1 per cent of water may occur normally in the vehicle. A small percentage, 1 to 3 per cent, may be incorporated into the paint by the manufacturer under the belief that it secures better penetration when applied to surfaces that are slightly damp, and also that it will prevent the pigment from settling and becoming hard in the can. Oftentimes, however, large quantities are introduced for the purpose of cheapening the product. The water may be added to the paint and prevented from separating out by forming an emulsion with the oil by the aid of an alkali, or by grinding it into the pigment, using an adhesive, such as glue or casein. In the first case the nature of the ash left on burning some of the separated vehicle will indicate whether an alkali has been used or not. In the second case the vehicle will yield less than 1 per cent of water when distilled with a dry, inert substance such as sublimed lead, as the water remains with the pigment.

21. Detection. Water may be tested for qualitatively in light-colored paints by rubbing with a little eosin on a glass plate. If water is present the paint will take on a strong pink color, otherwise the color will remain practically unchanged. If the paint contains considerable coloring material, rendering the eosin inapplicable, a weighed strip of gelatine may be immersed in the paint for several hours. If water is present the gelatine will soften and increase in weight,

the adhering paint being removed by the use of petroleum ether and drying for a minute or two between sheets of filter paper. An immersion of the gelatine for 18 to 24 hours will show the presence of water in a paint containing as little as 2 per cent.

22. **Estimation of water with amyl reagent.** This method, worked out by the author in his laboratory, has given excellent results, not only in mixed paints but also in paste and semi-paste goods. The determination requires only a few minutes, and as the combined water of the white lead is not driven off there is no correction to be applied.

23. **Preparation of amyl reagent.** This method has also given admirable results when applied to the determination of water in rosin oil and in varnishes contaminated with water. The components of the amyl reagent — amyl acetate and amyl valerianate — should be as pure as possible, and unless of specified purity an inferior grade is apt to be obtained which will yield unreliable results. Fritsche Brothers, New York City, have furnished the most satisfactory article the author has been able to secure. The amyl acetate and valerianate should be washed before mixing with at least two changes of pure distilled water at room temperature. This can readily be accomplished in a large separatory funnel. Washing with water will remove practically all the impurities, and such as may remain will be saturated at that temperature. The reagent is prepared by mixing 5 parts of amyl acetate with 1 part of amyl valerianate.

24. **Determination.** About 100 grams of the thoroughly stirred sample of paint are weighed into a flat-bottomed, 200–250 c.c., side-necked distilling flask. Add 75 c.c. of the amyl reagent and with a gentle

rotary motion secure a thorough mixing of the contents of the flask. Connect with an upright condenser and distill over about 60 c.c. of the reagent into a cylinder graduated into tenths of cubic centimeters. When the larger portion of water has passed over, the upper portion of the flask should be warmed gently with the naked flame, in order to expel the small portion of moisture that will have collected on the sides of the flask. The distillation should then be continued until the requisite amount of reagent has distilled over. The percentage of water can then be easily read off from the graduated cylinder and the contents of the distilling flask will be sufficiently liquid to insure easy removal. With paints high in volatile oils the volume of the distillate should be increased to at least 75 c.c.

25. **Practical example.** The following determination with a paint of known water content indicates the satisfactory nature and accuracy of this method.

White lead	115 grams
Linseed oil	40 grams
Turpentine	10 grams
Water	6 grams

were thoroughly mixed, introduced into a side-necked distilling flask, 75 c.c. of the prepared amyl reagent added, and the mixture agitated until of uniform consistency. The following distillation figures were obtained:

Temperature.	Water.	Amyl Reagent and Turpentine.
Deg. C.	c.c.	c.c.
92–110	5.5	16
110–125	0.9	13
125–140	0.0	18
140–145	0.0	14
	6.4	61

The same mixture without the addition of water gave 0.3 c.c. of water when run as a blank.

Theoretical percentage of added water	3.51
Percentage of water obtained (corrected)	3.56

Toluene is preferred by some chemists instead of the amyl reagent; its use for this purpose is not recommended by the author as the results are almost invariably low.

26. Estimation of water by distillation with inert pigment. This method has found a wide use among paint chemists. It is best carried out by using a retort, the neck of which forms the inner tube of a condenser, the outside tube being a Welsbach chimney. One hundred grams of the paint is weighed into an aluminum beaker and mixed with a thoroughly dried, inert pigment like silica or sublimed lead until it ceases to be pasty, and then transferred to the retort, which is heated in an oil bath, the water being collected in a graduate calibrated to fifths of cubic centimeters. Toward the end of the distillation, the temperature of the contents of the retort being raised to 200° C., a very slow current of air or illuminating gas is admitted to the retort through a tube passing nearly to the surface of the pigment. This will carry over the last traces of moisture.

27. Use of illuminating gas. It is advisable to pass the illuminating gas through a wash bottle containing sulphuric acid, which not only serves to remove moisture but acts as an indicator for the rate of flowing gas. The heating should be continued for at least two hours at the above temperature to insure the complete removal of the combined water from the basic carbonate of lead which may be present. This should be

deducted from the total amount of water obtained by multiplying the basic carbonate present by 2.3 per cent, which represents the average per cent of combined water in white lead.

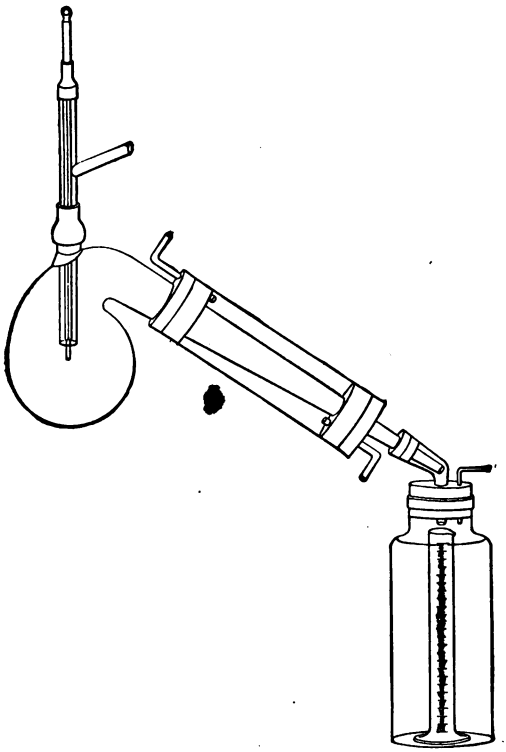

FIG. 4. — ESTIMATION OF WATER.

28. **Combined water.** It is impossible to remove the combined water by this method without decomposing part of the lead hydroxide of the white lead, as the water of combination begins to split off at 110° to 120° C., the total combined water being driven off at 150° C. with 6 hours heating with little or no loss of

carbon dioxide. An exposure of 4 hours at a temperature of 175 degrees results in the loss of all the water and a slight amount of carbon dioxide; at 200 degrees an exposure of 2 hours is sufficient to remove all the combined water and about one-quarter to one-third of the carbon dioxide.

In each case a blank should be run in order to ascertain that the inert pigment and illuminating gas are free from condensible moisture.

The author believes that a current of air obtained by the use of an aspirator is preferable to the use of illuminating gas, as with the latter there is the possibility of the formation of water from the hydrogen of the illuminating gas and the lead oxide present, if the temperature is raised too high.

29. Analyses. Eighty mixed paints analyzed by the author, white and gray shades, gave a water content calculated on the basis of total vehicle, as follows:

Amount of Water.	Number of Paints.
0 to 1 per cent	26
1 to 3 per cent	25
3 to 6 per cent	5
6 to 10 per cent	3
10 to 24 per cent	21

CHAPTER III.

WATER EMULSIONS AND EMULSIFIERS.

30. Occasionally it devolves upon the paint chemist to determine the agents used for securing and maintaining the emulsion of oil and water in paints and for preventing the hardening of paste goods, such as combination leads, etc.

31. **Necessity of an emulsion.** The use of water in paints has been a much discussed question. The majority of paint manufacturers have maintained that the addition of a certain amount of water is essential for the preparation of a high-grade paint, in order to prevent the pigments from settling hard in the bottom of the can, in which case there is much trouble and difficulty experienced in "breaking up" the paint when desired for use. As regards this contention the author believes the manufacturers are in the right, that better results are secured by the use of a small percentage of water in a paint high in lead and zinc. The line of demarcation, however, between the amount that can be considered legitimate for this purpose and that which may be considered as added for adulteration or cheapening, is by no means well defined. The author's experience has led him to believe that the true purpose of the addition of the water is best served by using an amount not exceeding 3 per cent of the vehicle present, and that any amount in excess of 5 per cent may be regarded as having been added for cheapening the product.

32. **Impairment of service value.** The addition of any considerable percentage of water unquestionably reduces the service value of a paint, but it is more often the materials used with the water to obtain the emulsion that cause the greater harm. Any substance which is astringent in its action, or which will cause a partial saponification of the oil, or bring about reactions between the oil and the pigments present, materially reduces the wearing value of such paint, and the author can only regard the addition of such substances as willful adulteration.

33. **Classification.** We may therefore divide the emulsifying agents into two classes, — those which are inert and those which are more or less active.

The first class comprises such substances as:

Glue,
Casein (free from alkali),
Oleates of lead and alumina,
Turpentine,
Glycerine, and
Starch.

The second class:

Chloride of lime,
Sulphate of zinc,
Silicate of soda,
Carbonate of soda,
Caustic soda,
Lead acetate,
Borax, and
Phosphate of soda.

34. **Glue and Casein.** The presence of glue and casein may be detected by heating a small portion

of the pigment, secured by extraction with ether, in a small porcelain crucible and noting the odor given off, and comparing the same with that obtained by heating a mixed pigment to which a little glue or casein has been added. The amount present may be determined by running a nitrogen determination according to the Kjeldahl method and multiplying the nitrogen content by 6.37. About 10 grams of pigment should be used.

35. **Oleate of lead.** Oleate of lead is but rarely used, as it is the most expensive of all emulsifiers. The present methods for detection and estimation are unsatisfactory.

36. **Turpentine.** Turpentine is by far the best emulsifier to use, as it is itself a normal constituent of paint. The formation of a water-turpentine emulsion can best be accomplished by grinding into a paste a non-settling pigment like asbestine pulp (magnesium silicate) or china clay with a little linseed oil, adding water and turpentine. The following affords a base of uniform consistency and composition which can be added to any mix of pigments in any desired proportion:

150 lbs. China clay,
150 lbs. asbestine pulp,
21 gal. water,
4 gal. linseed oil,
2 gal. turpentine.

A formula like the above possesses much merit, as both china clay and asbestine pulp are especially valued for their non-settling qualities and acting in conjunction with the water will prevent any reasonable combination of pigments from settling hard, even when used in small quantity.

37. Glycerine. Glycerine and starch are often used in conjunction with each other, not only for the purpose of introducing water but to prevent the hardening of paste goods, such as combination leads. The following working formula illustrates their use:

500 lbs. white lead,
300 lbs. zinc oxide "xx,"
150 lbs. white mineral primer,
200 lbs. barytes,
½ oz. ultramarine blue,
¾ lb. glycerine,
1 lb. starch (powdered),
15½ gal. linseed oil.

38. Chloride of lime. This product, while one of the most powerful emulsifying agents, is the most harmful to use owing to its astringent action on linseed oil. Just what the chemical reactions are which it enters into are difficult to determine, and it is difficult if not impossible to prove its presence in the majority of paints in which it is used except as indicated by failure to give satisfactory service value.

39. Sulphate of zinc. The evil effects of sulphate of zinc have been fully discussed by the writer in his work devoted to Zinc and Lead Pigments, Chapters XVI and XVII; therefore they need not be discussed here.

40. Carbonate of soda and caustic soda. These two substances are perhaps more generally used than any of the others. The conversion of a portion of the linseed oil into a water-soluble soap necessarily results in decreasing the life or wearing value of the paint in which the above ingredients may be used. Their presence may be judged by incinerating a small portion of the vehicle and examining the nature of the ash obtained.

41. Acetate of lead. The use of acetate of lead as an emulsifying agent cannot be commended. It acts as an astringent on the oil, although its effect is probably not so severe if it is incorporated into the paint subsequent to its passage through the mill as it would be if it were added in the original mix. A warm mill running under a suitable tension will cause any appreciable amount of acetate of lead to act vigorously on the linseed oil, causing a more or less pronounced hardening in the package as well as diminishing the life of the paint.

42. Borax and phosphate of soda. These products are usually used with carbonate of soda or caustic soda. The following is a much used formula:

Phosphate of soda	6 lbs.
Bicarbonate of soda	6 lbs.
Water	40 gal.

Both of these substances can be detected by the well-known qualitative tests.

43. Combination emulsifiers. Frequently a combination of several strong emulsifiers is used. The following formula has had an extensive use by several large manufacturers:

Chloride of lime	100 lbs.
Zinc sulphate	25 lbs.
Lead acetate	25 lbs.
Carbonate of soda	225 lbs.
Water	1200 gal.
Wood alcohol	30 gal.

The above materials are dissolved separately, the solution of zinc sulphate and of lead acetate being added to the chloride of lime solution (hot), the soda solution added, and finally the alcohol, which is added

for the purpose of keeping the paint in storage from freezing in winter. The above solution will emulsify excellently with equal quantities of linseed oil. The use of a formula of this type cannot be beneficial to the paint.

CHAPTER IV.

ESTIMATION OF LINSEED OIL AND ITS ADULTERATION IN MIXED PAINTS.

44. Separation of the volatile oils. The clear oil obtained by settling or with the aid of the centrifuge is weighed and introduced into a suitable-sized Erlenmeyer flask connected with a rather large condenser. The contents of the flask are brought to 130° C. by means of an oil bath, and a current of steam as dry as possible is conducted through the oil. The volatile oils rapidly distill over and are collected in a weighed, short-stemmed, separatory funnel, the water being drawn off from time to time as may be necessary. Severe frothing during the distillation indicates that an emulsifying agent, such as caustic soda or carbonate of soda, has been used. The frothing can be overcome by the addition of a few cubic centimeters of dilute sulphuric acid to neutralize the alkali used. The distillate is allowed to stand for several hours to insure the complete separation of the water, which is then drawn off and the volatile oils weighed and bottled for subsequent examination. The aqueous portion of the distillate will inevitably carry with it a small quantity of volatile oil, but the quantity will be slight, amounting to about 0.4 gram per 100 c.c. of water distillate. After obtaining the percentage of volatile oil the linseed oil is calculated by difference, by subtracting from 100 the percentages of volatile oil and water present in the paint.

The linseed oil, after being freed from the volatile oils, is allowed to stand, tightly corked, for several hours

in a warm place until thoroughly settled, and may then be tested for the presence of other oils.

45. **Presence of driers.** The linseed oil thus obtained will contain the Japan or drier solids present in the paint, which will usually be of a rosin nature. In the cheaper class of paints, and especially when linseed oil commands a high price, the manufacturer will often obtain relief by the use of a liberal percentage of a cheap benzine drier having a rosin base.

46. **Specific gravity.** Determine the specific gravity by means of a pycnometer or a Westphal balance.

The specific gravity may be taken at room temperature and calculated to 15.5° C.

Correction for 1° C. = .000650,
Correction for 1° F. = .000361.

The accepted limits for pure raw oil at 15.5° C. are 0.930 to 0.936 and for boiled oils 0.937 to 0.945. A low specific gravity may indicate:

a. Mineral oils.
b. Cottonseed oil.
c. Corn oil.
d. Soya-bean oil.

A high specific gravity may indicate:

a. Rosin or resinous products.
b. Rosin oils.
c. China wood oil.
d. Excessive heating or unusual addition of driers.

47. **Spot test.** One or 2 c.c. of the oil are poured on a porcelain plate and a drop of concentrated sulphuric acid is added carefully. If pure, the spot formed will bear a marked resemblance to a begonia leaf. If rosin

or rosin oil be present a black, gummy mass immediately results; cottonseed oil gives a spot without the characteristic markings of the linseed-oil spot. Mineral oils give a scum band, rapidly spreading out over the surface from the drop, the margin of the band being uniformly circular. Fish oils give a similar reaction, but the margin of the band is not at all uniform and may be readily distinguished from mineral oils. With a little practice and working with oils of known composition this test can be relied upon to detect any appreciable adulteration with the above oils.

48. **Mineral oils.** The spot test for petroleum products may be confirmed by allowing a sample of the oil to flow down a sheet of glass the other side of which has been painted jet black. If petroleum products are present even in a minute quantity, the sample will exhibit the "bloom" characteristic of mineral oils. A standard sample should always be run for comparison. It is possible to remove the "bloom" of mineral oils by the use of nitrobenzine, nitronaphthalene, or similar compounds, but the author is of the belief that this is very seldom resorted to in the paint industry.

49. **Quantitative estimation of mineral oil.** Quantitatively the mineral oil may be estimated by saponifying 10 grams of the oil with alcoholic potash for 2 hours, using a return condenser. The alcohol is distilled off and the soap dissolved in 75 to 100 c.c. of water, transferred to a separatory funnel, and 50 c.c. of ether added. The liquids are then shaken, avoiding the formation of an emulsion as far as possible. The aqueous solution is then drawn off, the ethereal layer washed with a few cubic centimeters of water to which a little caustic potash has been added, and poured into a weighed flask. The soap solution is then returned

to the separator, and twice extracted with ether in the same way as before.

The combined ethereal solutions are distilled off on the water bath, the flask dried and weighed. The increase in weight represents the amount of unsaponifiable matter, and unless rosin oil is present, represents the mineral oil with the exception of about 2 per cent, the average amount of unsaponifiable matter in linseed oil.

50. Separation of mineral oil from rosin oil. The mineral oil may be separated from the rosin oil in the unsaponifiable material by heating 50 c.c. of nitric acid of 1.2 specific gravity to boiling in a flask of 700 c.c. capacity, the source of heat removed, and the unsaponifiable material added. The flask is then heated on the water bath with frequent shaking for about one-half hour, and 400 c.c. of cold water added. After cooling, 50 c.c. of petroleum ether is added and the flask agitated, the mineral oil is dissolved, while the resinous matters remain in suspension. The liquid is then poured into a separatory funnel, leaving behind as much of the resinous material as possible. After settling, the aqueous liquid is drawn off and the ethereal layer poured into a weighed flask. Another portion of petroleum ether is added to the rosin remaining in the flask, and allowed to act upon it for about ten minutes, when it is added to that in the weighed flask. After distilling off the ether the oil is weighed. Mineral oils lose about 10 per cent when treated with nitric acid in this way, and hence the weight of the oil found must be divided by 0.9 in order to find the amount present in the sample analyzed.

50a. The Outerbridge test for mineral oil and rosin oil. A few drops of the oil to be tested are placed between

two plates of clear glass, placed against a black background and examined by reflected light from an *enclosed arc lamp*, adjusted to show a faint rosy light in addition to the powerful white light. The presence of mineral oil is evidenced by a greenish fluorescence, and rosin oil by a bluish fluorescence. Even the so-called debloomed oils show up strongly under this test. By preparing a set of standards of known composition as to percentages of mineral or rosin oils, and judging the sample under examination by comparison, reducing it, if necessary, with a known amount of pure vegetable oil until it corresponds in fluorescence with one of the standards, the approximate percentage of rosin or mineral oil may be determined. For this purpose 50 c.c. oil test bottles may be used. The value of the test depends on the enormously intensified fluorescence due to the particular source of light employed.

51. **Cottonseed oil.** This oil is seldom found in house paints, but is often used in the cheaper class of barn paints. The spot test may be confirmed by the Halphen test, the apparatus required being a large test tube with a condensing tube and a brine bath; the reagent employed being a 1.5 per cent solution of sulphur dissolved in carbon bisulphide with an equal volume of amyl alcohol added. Equal volumes of the oil and reagent are heated in a steam bath at first, and, after the violent boiling has ceased, in the brine bath at 105–110° C. for about 30 minutes. As little as 1 per cent of cottonseed oil will give a crimson wine coloration. Cottonseed oil heated to 250° C. does not respond to this test.

Quantitatively, the amount of cottonseed oil can only be approximated in a very general manner by means of the iodine values.

Let x = percentage of one oil and
y = percentage of the other oil,
m = average iodine value of pure oil x,
n = average iodine value of pure oil y, and
I = iodine value of sample under examination,

then $$x = \frac{100\,(I - n)}{m - n}.$$

52. **Corn oil.** This oil gives a spot test much resembling that given by linseed oil, but may be detected in linseed oil, if in quantity, by the following test: Dilute with four volumes of benzine, add one volume of strong nitric acid, shake. Linseed oil turns a white color, while corn oil turns a reddish orange.

Quantitatively corn oil can be estimated only approximately when in linseed oil, by the same method used for cottonseed oil.

53. **Fish oils.** In addition to the spot test these oils may be detected by rubbing a little of the sample vigorously between the palms of the hands. Fish-oil mixtures give the characteristic odor of oils of this class.

54. In case of doubt the Eisenschyml test[1] may be used: One hundred drops of the oil are dissolved in 6 c.c. of a mixture containing equal parts of chloroform and glacial acetic acid. Bromine is added drop by drop until the brown coloration remains. After 10 to 15 minutes the test tube is placed in a beaker containing boiling water. Linseed oil and other vegetable oils, such as China wood oil, cottonseed oil, corn oil, etc., will clear up completely within a few seconds, while fish oils will remain cloudy and precipitate an insoluble bromide at the bottom of the tube after a short

[1] J. Ind. and Eng. Chemistry, Feb., 1910.

time. With a little practice 5 per cent of fish oil is clearly recognizable.

In the case of boiled linseed oil it is necessary to remove the metallic constituents before adding the bromine. This is preferably done by shaking with a 10 per cent solution of nitric acid saturated with potassium nitrate.

In mixtures with linseed oil the amount present can only be determined crudely, by means of the "rise of temperature" with sulphuric acid with the Maumené apparatus described under the analysis of the volatile oils (Allen found the rise of temperature with sulphuric acid to be 104 to 111 in the case of linseed oil, and 126 in the case of menhaden oil), or else by weighing the insoluble bromides according to the procedure described by Eisenschyml. Fish oils are used only to a limited extent in paints.

55. Rosin and rosin oils. These products are best detected qualitatively by means of the Liebermann-Storch reaction, which is of sufficient delicacy to detect the presence of even very small quantities of rosin oil or rosin drier in boiled oil. Shake 1 to 2 c.c. of the oil under examination in a test tube with acetic anhydrides at a gentle heat, cool, pipette off the anhydride, and place a few drops on a porcelain crucible; cover, and add one drop of sulphuric acid (34.7 c.c. sulphuric acid and 35.7 c.c. water) so that it will mix slowly. If rosin or rosin oil is present a characteristic violet, fugitive color results. Certain fish oils will give a very similar color, but if present are easily detected by the fishlike odor of the oil on warming.

Old samples of pure boiled oil give a color that might be easily mistaken for rosin or rosin oils; in such cases it is best to warm the oil with alcohol so as to

extract the bulk of rosin present and test the alcoholic extract. Rosin may be more completely separated and estimated by Twitchell's process (J. Soc. Chem. Ind., 1891, 10, 804) or by Gladding's method (Amer. Chem. J., 3, 416). This process depends upon the solubility of silver resinate in ether, while the silver salts of fatty acids are insoluble.

56. **Soya-bean oil.** This oil has come into use quite largely during the last two years. Its chemical and physical properties are so nearly like those of linseed oil that it is difficult to detect it with certainty when mixed with linseed oil. In such mixtures the *spot test* exhibits a yellowish-green fluorescent color which is clearly recognized, but in the presence of a rosin drier this reaction is masked. When used to adulterate linseed oil an excessive amount of drier is usually added in order to overcome the slow drying of the soya-bean oil. Unlike linseed oil it does not bleach when strongly heated, but becomes several shades darker.

57. **Constants of soya-bean oil.**

Specific gravity	0.923–0.924
Acid number	190
Saponification number	188–188.5
Iodine number	127–136
Average iodine number	131

Often as much as 25 per cent of soya-bean oil may be added to linseed oil before the iodine number will be lowered sufficiently strongly to indicate such adulteration. However, if the iodine number is below 170 (Hübl) the presence of soya-bean oil may be strongly suspected. The oxygen absorption test will also yield information of value.

58. In the preparation of gloss paints a little varnish is added, the gums of which might be mistaken in the

above tests for rosin. In the cheaper paints a large excess of rosin is used in the resinate drier added. An easy method of detecting rosin and other resins and estimating the relative amount present is to stir up about 100 grams of the paint with 500 c.c. petroleum ether, allow to stand 24 hours in a cold place, siphon off the ether, and examine the skin formed on top of the pigment. This will harden in the course of another day so that it may be removed, placed on a watch glass, washed free of adhering pigment with more petroleum ether, and dried. The color and other physical properties will enable one to judge whether it is rosin or some of the other varnish gums.

59. **China wood oil.** The constants of China wood oil run quite uniform. The Hanus iodine method gives an iodine number abnormally high. The Hübl modification yields the best results, a 6-hour absorption being sufficient.

Specific gravity	0.941–0.943
Free acid value	4–4.5
Saponification number	190.8–191
Hübl iodine number	163–175

CHAPTER V.

DETERMINATION OF THE PURITY OF LINSEED OIL.

60. The paint chemist is frequently required to pass on the purity and quality of linseed oil, both raw and boiled, and must therefore determine its analytical characteristics with much care. The following example relative to a pure raw linseed oil is illustrative of the data usually required:

Specific gravity at 60° F. (15.5° C.)	0.9334
Iodine value	174.
Unsaponifiable matter	1.1 per cent
Saponifiable value	191.8
Acid value	2.8
Rosin test	Negative
Time of drying, 50 hours as against 52 hours with standard sample	
Loss at 100° C.	0.10 per cent
Color, odor, and taste similar to standard.	

The above determination can often be supplemented with advantage by data derived from the following estimations:

Flash test.	Oxygen absorption.
Maumené figure.	Bromination figure.
Refractive index at 15° C.	Hexabromide test.

61. **Specific gravity.** The specific gravity of a raw linseed oil should lie between 0.930 and 0.936, and that of boiled linseed oil between 0.937 and 0.945. All adulterants except rosin and rosin oil would lower the specific gravity.

62. **Determination of the iodine number.** The newer Hanus method for the estimation of the iodine number

is to be preferred to the older standard Hübl method, as the Hübl solution rapidly loses strength on standing and is very slow in its reaction. Nearly every chemist using it employs a modification of his own, especially as regards the time for the solution to remain in contact with the fat or oil, and hence very different results may be obtained on the same oil or fat by different investigators. Comparative tests by the two methods made in this laboratory gave results which varied only a few tenths of one unit.

63. **Preparation of reagents.** *Iodine solution.* Dissolve 13.2 grams of iodine in 1000 c.c. glacial acetic acid (99.5 per cent acid, showing no reduction with bichromate and sulphuric acid); add enough bromine to double the halogen content determined by titration — 3 c.c. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

Decinormal sodium thiosulphate solution. Dissolve 24.8 grams of chemically pure sodium thiosulphate, freshly pulverized, as finely as possible and dried between filter or blotting paper, and dilute with water to one liter at the temperature at which the titrations are to be made.

Starch paste. One gram of starch is boiled in 200 c.c. of distilled water for ten minutes and cooled to room temperature.

Solution of potassium iodide. One hundred and fifty grams of potassium iodide are dissolved in water and made up to one liter.

Decinormal potassium bichromate. Dissolve 4.9066 grams of chemically pure potassium bichromate in distilled water and make the volume up to one liter at the temperature at which the titrations are to be made.

The bichromate solution should be checked against pure iron.

64. **Determination.** *Standardizing the sodium thiosulphate solution.* Place 20 c.c. of the potassium bichromate solution, to which has been added 10 c.c. of the solution of potassium iodide, in a glass-stoppered flask. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color has almost disappeared. Add a few drops to the starch paste, and with constant shaking continue to add the sodium thiosulphate until the blue color just disappears.

65. **Weighing the sample.** Weigh about 0.5 gram of fat or 0.250 gram of oil on a small watch glass or by other suitable means. With drying oils which have a very high absorbent power 0.100 to 0.200 gram should be taken. The fat is first melted, mixed thoroughly, poured onto the crystal, and allowed to cool. Introduce the watch crystal into a wide-mouthed 16-ounce bottle with a ground-glass stopper.

66. **Absorption of iodine.** The fat or oil in the bottle is dissolved in 10 c.c. of chloroform. After complete solution has taken place, 25 c.c. of the iodine solution are added. Allow to stand with occasional shaking for 30 minutes. The excess of iodine should be at least 60 per cent of the amount added.

67. **Titration of the unabsorbed iodine.** Add 10 c.c. of the potassium iodide solution and shake thoroughly, then add 100 c.c. of distilled water to the contents of the bottle. Titrate the excess of iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color

has entirely disappeared. Toward the end of the reaction stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

68. Setting the value of the iodine solution. At the time of adding the iodine solution to the fat two bottles of the same size as those used for the determination should be employed for conducting the operation described above, but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments should be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid has a very high coefficient of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

69. A freshly prepared linseed oil will have an iodine value of about 185 to 187; this will rapidly drop to about 180, and when suitably aged will have decreased to about 175, although an old oil may have an iodine value as low as 170. This figure, however, should be regarded as the lowest acceptable limit. Boiled linseed oil as prepared for paint purposes will show an iodine number ranging between 160 and 175. Specially boiled oils may have an iodine number as low as 150.

70. IODINE NUMBERS OF VARIOUS OILS.

China wood oil	163–175
Corn oil	111–125
Cottonseed oil	101–117
Fish oil	148–180
Rosin oils	40– 65
Petroleum products	4– 20
Soya-bean oil	127–136
Turpentine	320–385

71. Unsaponifiable matter. The method for determining the unsaponifiable matter has been stated in the preceding chapter. A raw linseed oil should not contain more than 1.6 per cent of unsaponifiable matter and may contain as little as 0.5 per cent. A boiled oil will usually contain a slightly higher percentage, varying between the limits of 1 and 2 per cent.

The unsaponifiable matter in linseed oil consists essentially of waxes and complex alcohols.

72. Determination of the saponification value. This value is also spoken of as the Koettstorfer number and the saponification number. In each case it is equivalent to the number of milligrams of potassium hydroxide necessary to saponify one gram of the oil.

Two grams of the oil are weighed out into a small Erlenmeyer flask and saponified with 25 c.c. of half-normal alcoholic potash, by heating gently on a water bath, a funnel being inserted in the flask. When the saponification is complete a few drops of phenolphthalein are added and the excess of alkali titrated with half-normal hydrochloric acid. A blank determination of the strength of the alcoholic potash should be made at the same time.

The saponification value of raw linseed oil should lie above 189 and of boiled linseed oil above 197.

73. Determination of the free fatty acids in linseed oil. Ten grams of oil are weighed into a suitable-sized Erlenmeyer flask and 50 c.c. of neutral, aldehyde-free alcohol added. The mixture is heated to about 60° C. for a minute or two, then cooled and titrated with tenth normal alcoholic potash, using phenolphthalein as an indicator.

Oil made from moldy seed, or seed contaminated with mustard oil, or oil containing rosin, will have a

high acid figure. Pure raw oil should have a low acid figure; boiled oil will have a slightly higher figure.

74. **Preparation of aldehyde-free alcohol for alcoholic potash solution.** Dissolve 1.5 grams of silver nitrate in about 3 c.c. of water and add to a liter of alcohol in a glass-stoppered cylinder, mixing thoroughly. Dissolve 3 grams of pure potassium hydroxide in 10 to 15 c.c. of warm alcohol. Cool, pour slowly into the alcoholic silver nitrate solution, without shaking. The silver oxide is precipitated in a finely divided condition. Allow to stand until the precipitate has completely settled. Siphon off the clear liquid and distill. The distillate will be neutral and free from aldehydes, and will not darken when used as a solvent for potash.

The acid value of raw linseed oil is between 1 and 5 and of boiled linseed oil between 4 and 12, averaging between 7 and 8. Rosin and rosin in oils, if present, would materially raise the acid value, as rosin has an acid value of from 120 to 150 and rosin oil from 20 to 50.

75. **Free mineral acid.** Any free mineral acid in bleached oil is determined by washing a definite weight of oil with water, separating the water, and titrating the dissolved mineral acid present. Any mineral acid found will usually be sulphuric acid. Its presence is decidedly objectionable.

Varnish oil. A specially refined linseed oil is used in the manufacture of varnishes, and it often devolves upon the paint chemist to pass on such oils. It is not safe to judge the color of the oil from the sample as received, but it should be heated in a beaker slowly, to the temperature required in the varnish kettle, and after cooling the color should be compared with the standard sample, which should be kept in a dark place. Some varnish oils will bleach considerably

under heat, and others slightly or not at all. Varnish oils act on the varnish gums very differently in the varnish kettle; some flux with the gum easily; others combine with the gum with difficulty, requiring an excess of heat and a longer time to cook, often affording a varnish of quite dissimilar properties. It is therefore advisable for the chemist to have the varnish oil under examination thoroughly tried out in the varnish kettle before approving it.

76. Determination of the flash point of linseed oil. For exact flash-point figures rather expensive and complicated testers are needed, but for commercial tests that yield approximately the same figures a very simple apparatus may be used, consisting of a two-ounce crucible, a thermometer reading at least 300° C., and a small gas jet attached to a rubber tube, a flame about the size of a pea being used. The cup is filled two-thirds full of oil, the bulb of the thermometer suspended in it, and the oil slowly heated. The determination should be carried on in a place entirely free from drafts. At short intervals the gas flame is brought close, but without touching, to the surface of the oil, with a slow, sweeping motion. The first distinct puff of pale-blue flame that shoots across the surface of the oil indicates the flash point of the oil, and the temperature at which this occurs is noted.

Hurst states that linseed oil, whether raw or boiled, flashes at about 243° C., but these figures are considerably lower than those obtained in this laboratory, the raw oils flashing in the vicinity of 300° C. and the pure boiled oils from 275° to 300° C. Volatile oils used in the drier added to the oil lower the flash point considerably, 4 or 5 per cent of volatile oil lowering the flash point to about 250° C. The other vegetable oils, as

corn and cottonseed oils, flash at nearly the same temperature as linseed oil. Mineral oils, such as would be used for adulteration, flash at 193° to 216° C., rosin oils at 140° to 167° C. The presence of rosin oil would also be indicated by the strong odor of rosin given off during the heating. Benzine and turpentine when present in linseed oil rapidly lower the flash point according to the percentage present, having a flash point themselves but little above that of room temperature.

77. Correction to be applied to the thermometer reading.

Let N = Length of exposed thread of mercury expressed in degrees.

T = observed boiling point.

i = temperature of the auxiliary thermometer, the bulb of which is midway between the ends of the exposed mercury thread.

0.000154 = apparent coefficient of expansion of mercury in glass.

C = the correction in degrees.

Then $C = N(T - i) \times 0.000154$.

78. Linseed oil from inferior seed. This includes oil prepared from impure or adulterated seed, giving an oil of inferior quality, or, what is essentially the same thing, the screened foreign seeds are separately crushed and pressed and the resulting oil used to blend with a pure linseed oil. Such oils dry slowly and imperfectly, and the resulting film lacks the "hardness" given by the pure oils, and often give the consumer as just cause for complaint as the more grossly adulterated varieties.

79. When sold as raw oil, such oils usually have a greenish tinge, which disappears or is masked in the boiling. Chemically this form of adulteration is more difficult to detect than when other oils of distinctly

different chemical properties are used. With this class of oils the specific gravity, iodine number, saponification value, and unsaponifiable matter remain nearly normal, and the leading tests that may be applied to such suspected oils are their oxygen absorption power and the time required for drying. Both the per cent of oxygen and the rate of absorption will be found markedly lower, depending on the amount of foreign seed oil present. In order to obtain comparable results, a standard oil of known purity should be carried through the tests along with the suspected oil, as the weather conditions may seriously affect the rate of drying.

80. Spread about one gram of precipitated lead, weighed off accurately, on a somewhat large watch glass in a thin layer, and then allow to fall onto it from a pipette 0.6 to 0.7 gram (not more) of the oil to be tested, placing each drop on a different portion of the lead and taking care that the drops do not run into one another. Then allow the watch glass to stand at the ordinary temperature in a place exposed to light and protected from falling dust. Weigh at frequent intervals in order to note the rapidity with which the oil is absorbing oxygen and to determine accurately when the oil ceases to gain weight. The lead powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum.

81. Instead of precipitated lead, thin aluminum plates 3 inches by 6 inches may be used. The plates are weighed and 0.1 gram or 0.2 gram of oil rubbed over the plate, giving a thin, uniform film, weighed, set aside in a dust-free place, and the increase in weight noted from time to time.

The oxygen absorption figure of a freshly prepared linseed oil is usually between 18 and 19 per cent. This percentage will diminish somewhat during the aging process, but should not go below 16. On the other hand, a boiled oil may have an oxygen absorption as low as 14 per cent but will average about 16 per cent. The oxygen absorption of oils added as adulterants and weed seed oils which may be present decrease the oxygen absorption value.

82. Composition of linseed oil foots.[1] The foots from linseed oil, manufactured by the naphtha extraction process, after centrifuging, contained 75.8 per cent linseed oil, the extraction being conducted with carbon disulphide. The insoluble portion contained:

	Per cent.
SiO_2	34.38
CaO	7.98
MgO	8.39
P_2O_5	46.50
K_2O	Present
	97.17

The foots from an hydraulic pressed linseed oil contained:

	Per cent.
SiO_2	None
CaO	3.26
MgO	4.99
K_2O	10.27
P_2O_5	81.08
	99.08

[1] Eisenschyml, J. Ind. and Eng. Chem., Jan., 1910.

CHAPTER VI.

DETERMINATION OF THE PURITY OF LINSEED OIL (Continued).

83. Determination of the bromine absorption figure, McIlhiney's method.[1] The advantage of this method is that the absorption of halogen by addition is determined separately from the absorption by substitution, resulting in additional information as to the nature of the substance.

The process as at present used is as follows: A quantity of the oil to be analyzed is weighed into a glass-stoppered bottle, 10 c.c. of carbon tetrachloride added to dissolve the oil, and 20 c.c. of third-normal bromine in carbon tetrachloride added from a pipette. It is not found necessary in filling the pipette with bromine solution to use any special arrangement to prevent the introduction of bromine vapor into the mouth. Only a rubber tube is necessary. Another pipette full of solution should be added to 10 c.c. of carbon tetrachloride, and this blank titrated with thiosulphate to determine the strength of the bromine solution. The test itself need be allowed to stand only one or two minutes before adding 20 to 30 c.c. of 10 per cent solution of potassium iodide, the amount necessary depending upon the excess of bromine present. An excess, of course, does no harm. In order to prevent any loss of bromine or hydrobromic acid which would probably occur on removing the stopper of the bottle, a short piece of wide rubber tubing, of the sort used for Gooch cru-

[1] J. Am. Chem. Soc., XXI, 1084.

cibles, is slipped over the lip of the bottle so as to form a well around the stopper. It is advisable, also, to cool the bottle by setting it into cracked ice in order to produce a partial vacuum in the interior. Into the well formed by the rubber tubing is poured the solution of potassium iodide and the stopper opened slightly. If the bottle has been cooled with ice the iodide solution will be sucked into the bottle, and if it was not cooled some of the air from the interior of the bottle will bubble through the iodide solution, being thereby washed, and allow the iodide solution to enter the bottle. When sufficient iodide solution has been introduced the bottle is agitated to insure the absorption of the bromine and hydrobromic acid by the aqueous solution. The iodine now present is titrated with tenth-normal sodium thiosulphate, and when the titration is finished 5 c.c. of a neutral 2 per cent solution of potassium iodate is added. This liberates a quantity of iodine equivalent to the hydrobromic acid formed, and on titrating this iodine the bromine substitution figure may be calculated. The solution of potassium iodate should be tested for acidity by adding a measured quantity to a solution of potassium iodide, and if any iodine is liberated it should be determined with thiosulphate and a suitable correction introduced into the calculation. The potassium iodide, the thiosulphate solution, and the water used should all be tested to see that they are neutral.

The action between bromine and oil appears to be practically instantaneous as far as the bromine taken up by addition is concerned, but it seems likely that substitution is distinctly affected by the length of time that the oil and bromine are allowed to remain in contact.

84. BROMINE VALUES OF VARIOUS OILS.

	No.	Hübl Figure.	Bromine Calculated from Hübl.	Per Cent of Bromine Absorbed.	Bromine Addition Figure.	Bromine Substitution Figure.	Bromine from Hübl Divided by Bromine Addition Figures.
Raw linseed oil, several years old	1	166.9	105.2	98.4	95.4	1.5	1.103
Raw linseed oil, several years old	2	157.3	99.1	99.2	92.0	3.6	1.000
Raw linseed oil	3	184.2	116.1	116.1	109.6	3.4	1.059
Do.	4	178.6	112.6	108.5	102.1	3.2	1.102
Do.	5	185.9	117.2	113.2	109.2	2.0	1.072
Do.	6	186.3	117.0	112.2	106.5	2.9	1.098
Do.	7	...	...	104.5	99.9	2.3	...
Do.	8	...	...	115.1	109.5	2.8	...
Do.	9	...	...	114.6	109.4	2.6	...
Average, omitting Nos. 1 and 2	...	183.8	115.7	112.0	106.6	2.7	1.083
Boiled linseed oil	1	180.4	113.7	106.0	100.8	2.6	1.126
Do.	2	183.3	115.5	110.8	105.8	2.5	1.091
Do.	3	...	...	105.4	101.2	2.1	...
Do.	4	...	...	110.0	103.2	3.4	...
Do.	5	...	...	109.8	105.2	2.3	...
Do.	6	...	...	113.6	103.0	5.3	...
Do.	7	...	...	109.2	103.8	2.7	...
Do.	8	...	...	110.8	101.0	4.9	...
Averages	...	...	...	109.5	103.0	3.2	...
Third-run rosin oil	1	...	...	197.6	16.4	90.6	...
Do.	2	63.9	40.3	92.3	7.7	42.3	5.231
"Mystic" brand rosin oil	...	...	...	93.7	6.3	43.7	...
"Java" boiled rosin oil	...	73.3	46.2	101.9	8.3	46.8	5.685
Corn oil	1	...	...	76.2	73.8	1.2	...
Do.	2	...	...	75.8	73.2	1.3	...
Do.	3	...	...	75.4	71.6	1.9	...
Averages	...	...	...	75.8	72.9	1.5	...

85. Estimation of rosin in mixtures of linseed oil and mineral oil. Twitchell's method. A weighed portion of the sample is saponified by boiling with alcoholic potash, and the alcohol is driven off by prolonged boiling after diluting with water. The unsaponifiable matter is shaken out with petroleum ether, as previously described under linseed oil, the remaining soap solution made acid yielding a mixture of fatty and rosin acids. Heat until the fatty acids have separated on top. Cool, break the cake of fatty acids with a glass rod, pouring off the aqueous solution. Treat the acids again with boiling water, cool, remove to a porcelain dish, and dry at 100° C. until freed from all traces of water.

Two to three grams of the mixed fatty and rosin acids are weighed off accurately and dissolved in a flask in ten times their volume of *absolute alcohol*, and a current of dry hydrochloric acid gas is passed through for about forty-five minutes or until the gas ceases to be absorbed. Allow to stand one hour, then dilute it with five times its volume of water and boil until clear. From this point the analysis may be completed volumetrically or gravimetrically.

86. Volumetrically. The contents of the flask is transferred to a separatory funnel and the flask rinsed out several times with ether. Vigorously shaking, the acid layer is run off and the remaining ethereal solution containing the rosin acids washed with water until the last trace of acid is removed. Fifty c.c. of alcohol are added, and the solution titrated with standard caustic potash, using phenolphthalein as an indicator. The rosin acids combine at once with the alkali, whereas the ethylic esters remain unchanged. The number of cubic centimeters of normal alkali used multiplied by 0.346 will give the amount of rosin in the sample.

87. **Gravimetrically.** The contents of the flask is mixed with a little petroleum ether, boiling below 80° C., and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off and the petroleum ether layer washed once with water, and then treated in the funnel with a solution of 0.5 gram of potassium hydroxide and 5 c.c. of alcohol in 50 c.c. of water. The ethylic esters dissolved in the petroleum ether will then be found to float on top, the rosin acids having been extracted by the dilute alkaline solution to form rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids collected as such, or preferably dissolved in ether and isolated after evaporating the ether. The residue, dried and weighed, gives the amount of rosin in the sample.

88. **Evaporation test.** This test will show very closely the amount of benzine added along with the drier in the preparation of boiled linseed oil.

Five grams of the oil to be tested are weighed into a small flat-bottomed evaporating dish and allowed to remain undisturbed at a temperature of 100° C. for three hours. The dish is then removed, cooled quickly, and immediately weighed. The loss in weight usually represents the greater portion of mineral oils, rosin oils, or other volatile matters present in the sample.

J. Hortvet, state chemist for Minnesota, states that:

"Of fifteen samples represented as raw linseed oil, when subjected to this test, eleven showed no loss in weight, while four gave losses amounting to less than 0.3 per cent. Of one hundred and ten samples represented as boiled oils, sixty gave losses above 2 per cent,

thirty-two showed no loss in weight, and of the remaining eighteen the loss was slight, seldom approaching 2 per cent. Forty-seven of the sixty samples which gave over 2 per cent loss were found to vary in specific gravity from 0.8835 to 0.9310. All samples not found adulterated by the usual tests showed a specific gravity of from 0.9310 to 0.9425, with the exception of one sample which had a specific gravity as low as 0.930, but by the other tests appeared to be straight raw linseed oil."

89. Hexabromide test.[1] The determination should be made in glass-stoppered weighing bottles about 6 inches high and 1 inch in diameter, weighing about 30 grams each. These bottles should be carefully dried and weighed. Weigh 0.3 gram of oil to be tested, add 25 c.c. of absolute ether, and cool to about 0° C. Add bromine drop by drop until a considerable excess is shown by the color of the solution. Stir constantly during the addition, which should be conducted very slowly, so as to avoid heating. Place tube in ice water for 30 minutes, then centrifuge for 2 minutes. The brominated oil is thrown to the bottom of the tube. The supernatant liquid is quickly decanted. Agitate the precipitate with 10 c.c. ice-cold ether centrifuge and decant; repeat this procedure twice, thoroughly cooling the precipitate and ether each time. Finally dry in steam oven for 30 minutes, cool, and weigh.

90. Linseed oil. The following specifications, recently adopted by one of the leading railroad companies, are as comprehensive as any that have come under the author's observation and may be regarded as typical of those used by discriminating purchasers of linseed oil:

[1] Proc. Am. Soc. for Test. Mat., Vol. IX, p. 152.

Material.

The material desired under this specification is the best grade of raw and boiled linseed oil, as shown by the following requirements:

Raw Linseed Oil.

1. This material must be a good quality of oil of a pale yellow color, made from No. 1 flaxseed, well clarified by settling and age, and must be unmixed with any foreign substance whatever.

2. It must not have a greenish color, produced by unripe or impure seed.

3. Its specific gravity must be between .930 and .937 at 60° F.

4. It must have a flash above 550° F. in an open cup tester.

5. It must contain less than one per cent (1%) of foots.

6. It must not lose more than one-tenth per cent (.1%) when heated at 212° F. for three hours.

7. Its saponification value must not be less than 187 or more than 195.

8. Its iodine value (Hübl's Method) must exceed 170.

9. It must dry without tackiness in less than 75 hours at 60° F. when a layer is spread over a vertical glass plate in uniform thickness and left in an enclosed room.

10. It must not contain more than one and one-half per cent (1.5%) of unsaponifiable matter.

11. Its acid value must not exceed 8.

12. Its specific temperature reaction (Thompson & Ballantyne Method) must not exceed 2.69, water = 1 being taken as the standard.

91. Boiled linseed oil.

1. This material must contain nothing but kettle-boiled pure linseed oil, and lead, or manganese oxides or borates, or both, in chemical combination, but not in suspension.

2. Raw oil mixed with turpentine or benzine dryer, known as "Bung Boiled" or "Bung-hole Boiled" will not be accepted.

3. Its specific gravity must be between .937 and .950 at 60° F.

4. It must show between two-tenths per cent (.2%) and five-tenths per cent (.5%) residue after ignition.

5. The salts of lead and manganese must not exceed four per cent (4%) by weight.

6. The total weight of linseed oil in the boiled oil must not be less than ninety-six per cent (96%).

7. It must not show a flash point below 500° F. in an open cup tester.

8. It must not contain more than one-half of one per cent (.5%) of volatile matter when heated at 212° F.

9. It must not contain foots or other suspended matter.

10. Its saponification value must exceed 187.

11. Its iodine value (Hübl's Method) must exceed 160.

12. Its acid value must not exceed 12.

13. It must dry without tackiness within 24 hours at 65° to 75° F. when a layer is spread over a vertical glass plate in uniform thickness and left in an enclosed room.

14. The unsaponifiable organic matter must not exceed two per cent (2%).

15. It must not contain raw linseed oil, mineral oil,

benzine, turpentine, benzene, rosin, rosin oil, maize or corn oil, fish oil, cottonseed oil, rape oil, or saponifiable and unsaponifiable oil, other than boiled linseed oil.

92. **Tests.** When a shipment is received, a single sample will be taken from a barrel at random and the shipment will be accepted or condemned upon the results of the above test Any standard test, in addition to those specified above, may be made to ascertain if the shipment meets the intent and requirements of this specification.

The above specifications require the use of a linoleate drier in the preparation of the boiled linseed oil. The author, however, can see no serious objection to the use of a properly prepared non-volatile resinate drier, as the amount that may be used cannot exceed 4 per cent, as stated in section 6.

CHAPTER VII.

ANALYSIS OF THE VOLATILE OILS.

93. Identification. The volatile oil distilled from the linseed oil, as previously described, may be tested qualitatively for spirits of turpentine, stump turpentines, rosin spirit, petroleum naphtha, and benzole by the following test:[1]

Shake in a test tube equal volumes of the turpentine to be tested and concentrated sulphurous acid until quite thoroughly mixed Set aside, noting the time of separation and the color of the two strata. Samples of known purity should be run alongside of the sample to be tested, and the time of shaking the samples should be as uniform as possible. Deadwood turpentine, if highly rectified, gives a reaction approaching that of livewood turpentines.

1. *American Turpentine.*

Separation takes place very slowly.
Upper Stratum — Opaque; milky white.
Lower Stratum — Translucent; milky white.
Odor — Slight terpene smell.

2. *Russian Turpentine.*

Quick separation.
Upper Stratum — Translucent; faint turbidity.
Lower Stratum — Clear and colorless.
Odor — Slight pungent smell.

[1] Scott's Test for Turpentines, Drugs, Oils and Paints, 1906.

3. *Deadwood Turpentine.*

Medium slow separation.
Upper Stratum — Opaque; light buff color.
Lower Stratum — Translucent; yellow-amber color.
Odor — Distinct tar smell.

4. *Livewood Turpentine.*

Medium quick separation.
Upper Stratum — Translucent; lemon-yellow color.
Lower Stratum — Clear and colorless.
Odor — Mild tar smell.

5. *Rosin Spirit.*

Medium slow separation.
Upper Stratum — Translucent; golden-yellow color.
Lower Stratum — Translucent; creamy-white color.
Odor — Pungent resin smell.

6. *Benzine (Petroleum Naphtha).*

Quick separation.
Upper Stratum — Clear and colorless.
Lower Stratum — Clear and colorless.
Odor — Sulphurous smell.

7. *Benzole.*

Quick separation.
Upper Stratum — Slight turbidity; faint yellow color.
Lower Stratum — Clear and colorless.
Odor — Benzole and sulphurous smell.

94. Estimation of petroleum products. If the qualitative test indicates the presence of live or deadwood turpentine in appreciable quantities, the amount of

petroleum product that may be present is best estimated as follows:

A measured quantity of the volatile oil is allowed to drop slowly into 300 c.c. of fuming nitric acid contained in a flask provided with a return condenser and immersed in cold water. A violent reaction takes place and the flask should be shaken occasionally. When all action has ceased the contents of the flask is poured into a separatory funnel and thoroughly washed with successive portions of hot water to remove the products of the action of the acid on the turpentine. The remaining petroleum oil is separated and measured or weighed.

95. Wood turpentine being absent, the amount of petroleum products may be very closely approximated by the "Sulphuric Acid Number."

The apparatus and materials required are a large test tube of considerable diameter, bedded in closely packed cotton, in a fiber mailing case of suitable size, a thermometer provided with a platinum flange attached to the lower end. The lower part of the flange is bent at right angles to the stem of the thermometer. A mailing case packed with cotton offers many advantages over the regulation asbestos fiber mixed with plaster of Paris, in that if the test tube is broken during the estimation the bottom of the mailing case may be readily removed and the acid-soaked cotton replaced at once with fresh, while the plaster of Paris composition has to be washed and dried out, an operation requiring several hours.

96. A neutral mineral oil is required, giving a rise when treated with sulphuric acid of not more than 3° C.; also a standard bottle of concentrated sulphuric acid kept for this purpose, and a sample of turpentine

known to be pure. Fifty c.c. of the neutral oil are pipetted into the large test tube, the temperature noted, and 20 c.c. of the acid, of the same temperature, added from the burette in a steady stream, stirring rapidly, meanwhile, with a uniform motion, to maximum temperature, which is noted. After cleaning and cooling the apparatus the experiment is repeated exactly as before, but with the addition of 10 c.c. of pure turpentine to the neutral oil. The rise in temperature is again noted. Similar determinations are made with mixtures of 50 per cent of turpentine and 50 per cent of benzine, and also of 75 per cent of turpentine and 25 per cent of benzine. Having thus ascertained standards for comparison, 10 c.c. of the sample under examination is carried through in exactly the same manner, the maximum temperature noted, and the per cent of turpentine and of petroleum product calculated. Commercially pure turpentines will give closely uniform results. Wood turpentines give lower figures, which approach those of turpentine the more carefully the product is prepared and purified. Rosin spirits give a rise of 7° to 10° C., benzine and benzole 3° to 8° C.

97. Determination of flash point and fire test of petroleum products, turpentine, etc. Covered testers. *New York State Board of Health Tester.* This instrument consists of a copper oil cup holding about 10 ounces heated in a water bath over a small flame. The cup is provided with a glass cover holding a thermometer. This cover also has a hold for the insertion of the testing flame.

The test should be applied as follows:[1]

"Remove the oil cup and fill the water bath with cold water up to the mark on the inside. Replace the

[1] Report New York State Board of Health, 1882, p. 495.

oil cup and pour in enough oil to fill it to within one-eighth of an inch of the flange joining the cup and the vapor chamber above. Care must be taken that the oil does not flow over the flange. Remove all air bubbles with a piece of dry paper. Place the glass cover on the oil cup, and so adjust the thermometer that its bulb shall be just covered by the oil.

"If an alcohol lamp be employed for heating the water bath the wick should be carefully trimmed and adjusted to a small flame. A small Bunsen burner may be used in place of the lamp. The rate of heating should be about two degrees per minute, and in no case should exceed three degrees.

"As a flash torch, a small gas jet one-quarter of an inch in length should be employed. When gas is not at hand employ a piece of waxed-linen twine. The flame in this case, however, should be small.

98. ANALYSIS OF VOLATILE OILS BY THE AUTHOR.

No.	Name of Oil.	Sp. Gr. at 22° C.	Odor.	Rise C.	Separation.	Lower Layer.	Upper Layer.
1	Terrabentine	.808	Petroleum	6°	Immediate	Clear	Slightly milky
2	Turpentine	.855	Camphor	52.5°	Rapid	Almost clear	Lemon, milky
3	Turpentine	.862	Oil	57.0°	Medium	Milky	
4	Off-color turpentine	.857	Characteristic turpentine	30.5°	Slow	Clear	Clear
5	Turpentine	.853	"	48.3°	Slow	Milky	Milky
6	Turpentine	.860	"	56.7°	Medium	Milky	Slight tinge of yellow
7	Wood-spirits turpentine	.859	Stump turpentine	52.8°	Slow	Deep lemon	Milky
8	Turpanli base	.862	Petroleum	1.0°	Quick	Clear	Clear

No. 1. Straight petroleum product.
No. 2. Wood turpentine.
No. 3. Commercially pure turpentine.
No. 4. Spirits of turpentine, containing about 50 per cent petroleum naphtha.
No. 5. Spirits of turpentine, containing about 15 per cent petroleum naphtha.
No. 6. Poorly rectified turpentine.
No. 7. Stump turpentine.
No. 8. Straight petroleum product.

99. "When the temperature of the oil in the case of kerosene has reached 85° F., the testings should begin. To this end insert the torch into the opening in the cover, passing it in at such an angle as to well clear the cover, and to a distance about half-way between the oil and the cover. The motion should be steady and uniform, rapid, and without any pause. This should be repeated at every two degrees' rise of the thermometer, until the thermometer has reached 95 degrees, when the lamp should be removed and the testings should be made for each degree of temperature until 100 degrees is reached. After this the lamp may be replaced if necessary, and the testings continued for each two degrees.

"The appearance of a slight bluish flame shows that the flashing point has been reached.

"In every case note the temperature of the oil before introducing the torch. The flame of the torch must not come in contact with the oil.

"The water bath should be filled with cold water for each separate test, and the oil from a previous test carefully wiped from the oil cup."

100. **Open testers.** *Tagliabue's open tester.* This instrument is similar to the preceding, except that it is smaller, the oil cup being of glass and without a cover. The water bath is filled as before. The oil cup is filled to within three thirty-seconds of an inch of the top. The heating flame is regulated to three-fourths of an inch in height, or to such a height that the temperature of the oil is raised two and a half degrees per minute until 97° F. is reached, when the test flame is applied and the testings are made every two degrees until the flash point is reached.

101. **Fire test.** The fire test is the temperature at

which an oil will give off vapors which when ignited will burn continuously. The cover is removed in the case of the closed tester, the heating being continued as described above. The flame may be extinguished by the use of a piece of asbestos board.

102. Excessive use of volatile oils. An excess of thinners or volatile oils is detrimental to the life of the paint. Sabin in his work on The Technology of Paint and Varnish writes as follows:

"Most of the failures of lead and zinc paints are due to the use of these volatile thinners (turpentine and benzine). If raw linseed oil is used, it may be desirable to add 5 per cent of a good drier. This should be pale in color, indicating that it has been made at a low temperature, and should be free from rosin. The latter is not an easy thing to detect, but if a fair price is paid, say $1.50 to $2.00 a gallon at retail, and freedom from rosin is guaranteed by a maker of good reputation, the buyer ought to feel safe."

103. The presence of a large amount of thinners renders the paint easier to brush out, and hence the tendency has been to increase the amount of thinners, especially benzine, because of its low cost, in mixed paints, resulting in the reducing of the linseed oil to a percentage below that required to give the proper life to the paint. The better class of paint manufacturers seem to consider 4 to 9 per cent of thinners sufficient for outside house paints.

Excluding the 21 paints containing 12 per cent of thinners and over, the average amount of thinners in the remaining 50 paints was 7.3 per cent. The paints high in thinners were in almost every case inferior paints, high in inert pigments.

Of seventy-one analyses of white and gray mixed

paints made by the author, the amount of thinners came between the following limits:

Per cent Thinners.	Number of Paints.
0 to 4	6
4 " 5	5
5 " 6	1
6 " 7	6
7 " 8	10
8 " 9	5
9 " 10	11
10 " 11	4
11 " 12	2
12 " 29	21

CHAPTER VIII.

TURPENTINE THINNERS.

104. Spirits of Turpentine. This product, which has long been known to the paint and varnish trade, possesses several commercial designations, such as "gum turpentine," "oil of turpentine," "turpentine," and "spirits of turpentine." Its source and distinctive properties are specifically set forth in the Pharmacopœia of the United States as follows: "Oil of turpentine: A volatile oil distilled from turpentine (a concrete oleo-resin obtained from *Pinus palustris* and other species of pinus)." "A thin, colorless liquid having a characteristic odor and taste." "Specific gravity 0.855 to 0.870 at 15° C. (59° F.). It boils at 155° to 170° C. (311° to 338° F.)." The United States Government under the Food and Drugs Act has ruled that a product to be entitled to the above designations — "spirits of turpentine," "turpentine," etc., — must comply with the pharmacopœial requirements above stated, and that oils obtained by distillation from resinous woods should be designated "wood" or "stump" turpentine.

105. Adulteration. The paint or varnish manufacturer who purchases direct from dealers engaged in the naval stores business will very rarely receive willfully adulterated turpentine, but will occasionally receive shipments of insufficiently refined turpentine containing various quantities of rosin and resinous matters. This form of adulteration is easily detected. On the other hand, the retail dealer and master painter who purchase from jobbing houses and traveling salesmen

are very liable to obtain an adulterated article. Recent investigations have shown that the adulteration of turpentine after it has been shipped from the primary markets is a much more common practice than has been supposed. Usually the adulteration has been accomplished with naphtha or other petroleum distillates, which, owing to their low price, makes this phase of the industry very profitable. The author believes that the adulteration of turpentine with rosin spirit or with wood turpentine is very rare, as the margin of profit is not large enough to make the proposition sufficiently attractive.

106. Specifications. The specifications adopted by the Navy Department Jan. 4, 1908, for spirits of turpentine are as complete as any that have come under the observation of the author:

1. The turpentine must be the properly prepared distillate of the resinous exudation of the proper kinds of live pine or live pitch pine, unmixed with any other substance; it must be pure, sweet, clear, and white, and must have characteristic odor.

2. A single drop allowed to fall on white paper must completely evaporate at a temperature of 70° F. without leaving a stain.

3. The specific gravity must not be less than 0.862 or greater than 0.872 at a temperature of 60° F.

4. When subjected to distillation, not less than 95 per cent of the liquid should pass over between the temperature of 308° F. and 330° F., and the residue should show nothing but the heavier ingredients of pure spirits of turpentine. If at the beginning of the operation it shows a distillation point lower than 305° F. this will constitute a cause for rejection.

5. A definite quantity of the turpentine is to be put

in an open dish to evaporate, and the temperature of the dish will be maintained at 212° F.; if a residue greater than 2 per cent of the quantity remains on the dish it will constitute a cause for rejection.

107. Flash tests. An open tester is to be filled within one-fourth inch of its rim with the turpentine, which may be drawn at will from any one can of the lot offered under the proposal. The tester thus filled will be floated on water contained in a metal receptacle. The temperature of the water will be gradually and steadily raised from its normal temperature of about 60° F. by applying a gas or spirit flame under the receptacle. The temperature of the water is to be increased at the uniform rate of 2° F. per minute. The taper should consist of a fine linen or cotton twine (which burns with a steady flame) unsaturated with any substance. When lighted it is to be used at every increase of 1 degree temperature, beginning at 100° F. It is to be drawn horizontally over the surface of the turpentine and on a level with the rim of the tester. The temperature will be determined by placing a thermometer in the turpentine contained in the tester so that the bulb will be wholly immersed in the liquid. The turpentine must not flash below 105° F.

108. Sulphuric acid test. Into a 30 c.c. tube, graduated to tenths, put 6 c.c. of the spirits of turpentine to be examined. Hold the tube under the spigot and then slowly fill it nearly to the top of the graduation with concentrated oil of vitriol. Allow the whole mass to become cool and then cork the tube and mix by shaking the tube well, cooling with water during the operation if necessary. Set the tube vertical and allow it to stand at the ordinary temperature of the room not less than half an hour. The amount of clear layer

above the mass shows whether the material passes test or not. If more than 6 per cent of the material remains undissolved in the acid this will constitute a cause for rejection.

109. Adulteration with petroleum products. Adulteration with any considerable quantity of a petroleum distillate will be indicated by a low specific gravity of the suspected sample, but if 10 per cent or less be present the gravity will be lowered only slightly and distillation through a LeBel-Henninger column should be resorted to and the specific gravity and index of refraction of the different fractions should be determined as described in the paragraphs devoted to wood turpentine in this chapter. The rise of temperature with sulphuric acid, of the different fractions as described in the preceding chapter, will give an approximation of the amount of petroleum distillate present.

If adulteration with wood turpentine be suspected, the quantity and character of the heavier fractions should be carefully determined.

110. Rosin spirit. If rosin spirit is suspected, the test proposed by Grimaldi may be made use of. Distill 100 c.c. of the oil of turpentine to be examined over a very small gas flame, and collect the fractions separately at intervals of 5 degrees of temperature. To the first five fractions an equal volume of hydrochloric acid is added, and a few granules of pure tin, and the whole well shaken and kept in a water bath for five minutes. The presence of resin spirit (pinolin) is indicated by a green color, which varies according to the percentage of resin spirit present. Further, one drop of each fraction is tested by mixing with 2 c.c. of Halphen's reagent (sulphur dissolved in carbon disulphide) and a little melted phenol dissolved in carbon tetrachloride.

A trace of bromine vapor is allowed to fall on the liquid, and in the presence of resin spirit a green color will develop within half a minute.

111. **Wood turpentine.** The use of wood turpentine is increasing rapidly. The different products offered under this heading are of a much more satisfactory nature than those offered for sale a few years ago. This improvement in quality is due to increased care in refining, thereby eliminating the objectionable impurities. As these wood turpentines are offered for sale at a price of from 2 to 10 cents below that of gum spirits, it is distinctly to the advantage of the manufacturer of paints and varnishes to use them, provided he can secure a well-refined article. Unfortunately, while the producers of wood turpentine are many, the amount produced by any one company is comparatively small, and it is usually impossible for a paint manufacturer to secure a steady and uniform source of supply. It therefore devolves upon the paint chemist to examine a considerable number of wood turpentines yearly, and to select those best suited for the purpose, or, in other words, to select those which more nearly resemble the gum spirits.

112. As is well known, wood turpentine is obtained by two methods, viz., by subjecting the stumps or mill waste to a destructive distillation, whereby the turpentine obtained is contaminated with the decomposition products from the breaking down of the rosin and the wood, which renders the refining of the turpentine a very difficult matter. In fact, a paint manufacturer will usually discriminate against a turpentine obtained by destructive distillation. The other process of obtaining wood turpentine is by steaming the chipped stumps or mill waste, thereby avoiding any serious

decomposition of the wood or rosin contained in it. On redistillation a turpentine product is obtained which has a pleasant odor, suggestive of pine wood, and which will distill largely within the accepted limits of the ordinary gum spirits, but which will contain a varying fraction of the heavier pine oils.

113. A suitably selected "Steam" turpentine is fully the equal of the gum spirits for mixed paints and for medium or slow-drying varnishes. For such quick drying varnishes as it is desirable to prepare with the aid of turpentine alone or with naphtha, a mixture of 40 per cent of gum spirits with 60 per cent of a steam wood turpentine is as desirable as the gum spirits alone.

114. **Valuation of wood turpentine.** The valuation of a wood turpentine aside from its odor will depend largely upon its distillation figures and the specific gravities of the fractions obtained. The more usual method of distilling with the aid of direct heat in a side-necked distilling flask is open to serious objection for two reasons: first, the portions that condense in the neck of the flask and drop down on the hot liquid below will cause a certain amount of "cracking" or decomposition, coloring the undistilled residue yellow; second, when only a small amount remains in the distilling flask the vapors become superheated, which may indicate a distilling temperature several degrees above the normal figure. Under the same conditions pure water can be made to indicate a distilling temperature of as high as 107° C., due to the superheating of the aqueous vapor.

115. **Distillation with steam.** The most satisfactory method of conducting the distillation is to use steam, and thus avoid direct heating altogether. By the use

of a LeBel-Henninger 5-bulb distilling tube or column the heavier fractions in the turpentine can readily be separated and their gravities examined, and the non-volatile residue can be examined as to color and percentage.

116. Author's modification. Three hundred cubic centimeters of the sample to be examined are placed in a 500 c.c. Erlenmeyer flask provided with a 5-bulb LeBel-Henninger column and with a steam supply tube extending nearly to the bottom of the flask. The contents of the flask are raised by direct heat to about 80 or 90° C. The source of heat is then removed and live steam admitted, the distillate being collected in a 100 c.c. graduated cylinder, which is changed as soon as the 100 c.c. mark is reached. This operation is continued until all the volatile portions have distilled over, and the number of cubic centimeters of turpentine and of water in each 100 c.c. cylinder is then noted.

117. Law governing distillation of mutually insoluble liquids. In the distillation of a mixture of two mutually insoluble liquids, each of which has a definite boiling point, it is a well-known fact that the mixture will distill at a constant temperature, in the ratio of the products of their respective vapor densities and vapor tensions, at the temperature of distillation. In the above case, when we have a mixture of water and gum turpentine, the ratio of distillation is approximately 60 parts of turpentine to 40 parts of water, the distilling temperature being about 94° C. This ratio holds only for that portion of the turpentine which distills with direct heat between 156° C. and 160° C. The heavier fractions require a much larger volume of water for their distillation.

118. Distillation figures of a gum turpentine. The following table illustrates the distillation results obtained with a gum turpentine slightly below average:

Fraction.	Mixed Distillate.	Turpentine.	Water.	Temperature.	Sp. Gravity at 22° C.
	c.c.	c.c.	c.c.	Deg. C.	
1	100	60	40	94	0.862
2	100	60	40	94.5	0.862
3	100	60	40	94.5	0.862
4	50	30	20	94.5	0.866
5	50	29	21	95.0	
6	50	25	25	95.5	0.867
7	50	18	32	97.0	0.871
8	100	12	88	97.5–98.5	.....
9	Non-volatile	6	.....	.....	.....

119. Distillation figures of a wood turpentine. A wood turpentine under similar treatment gave the following results:

Fraction.	Mixed Distillate.	Turpentine.	Water.	Temperature.	Specific Gravity at 22° C.
	c.c.	c.c.	c.c.	Deg. C.	
1	100	60	40	94.0	0.8600
2	100	60	40	94.5	0.8605
3	100	60	40	95.0	0.8610
4	100	60	40	95.0	0.8610
5	100	58	42	95.5	0.8615
6	100	47	53	96.0	0.8620
7	50	20	30	96.5	0.866
8	50	15	35	97.0	0.872
9	50	10	40	98.0	0.885
10	50	3	47	98.5	
11	Non-volatile	7	.....	.....	.....

Fraction No. 8 was of a straw color and Nos. 9 and 10 were yellow. This particular sample represented a rather high grade of a destructively distilled wood turpentine.

120. In order to conduct the distillation successfully and rapidly the apparatus required should always be kept set up ready for use. The specific gravities can

readily be determined with a Westphal balance, and it will be found that the entire operation can be conducted in the same length of time as is required for the more ordinary distillation. This method thoroughly differentiates the heavier fractions and leaves the residue uncontaminated with decomposition products such as are obtained when direct heat is applied. It is of course understood that the distillations should always be conducted under uniform conditions.

121. Detection of petroleum products. If there is any reason to suspect adulteration with petroleum products, such as benzine, petroleum spirits, or kerosene, the determination of the index of refraction of the different fractions and the rise of temperature with sulphuric acid will reveal even a very small percentage of adulteration.

122. Geer's modification. In cases of controversy or in court procedure, the modification worked out by Geer (U. S. Dept. of Agriculture, Forest Service, Circular 152), which is somewhat similar to the author's method, may be followed to advantage, as it is more elaborate and specific in its details. For ordinary commercial usage, however, it is somewhat lengthy and tedious in its application.

123. Standards of purity. It is well-nigh impossible to establish standards with regard to the amount of non-volatile matter permissible in a high-grade gum turpentine or of a heavy turpentine and non-volatile matter permissible in wood turpentine. The author has rejected numerous samples of gum turpentine containing non-volatile matters in excess of 1.8 per cent, as the non-volatile matter was of a distinctly resinous nature. In a wood turpentine the non-volatile matter should not exceed 2 per cent, nor contain more than 10 per

cent of a fractionated portion with specific gravity above 0.872. Usually each paint chemist will establish his own standards, based on his own experience. He should, however, keep for future reference a pint sample of each distinctive turpentine examined. These should be kept in a tightly closed can or in a bottle which has received a heavy coating of black paint in order to avoid the chemical changes caused by light. A variety of such samples, together with the data appertaining to them, color, odor, flash point, gravity, and distillation figures, including the specific gravities of the fractions and their indices of refraction, will enable the chemist to pass on, or place a comparative valuation on, any given sample rapidly and accurately.

124. The heavier turpentines. In the production of wood turpentine by steaming or by extraction a series of heavier terpene bodies are obtained. In some instances these are allowed to remain in the turpentine, and of course are readily detected and estimated by the fractionating method above described. Generally these terpenes are removed to a certain extent by the producer and placed on the market under some such name as *pine oil*. Like the wood turpentines found on the market several years ago, they differ greatly in value and desirability, no uniform standard having been established. The more desirable varieties have a mild, pleasant, fragrant pine odor, somewhat suggestive of camphor, and a specific gravity varying between 0.890 and 0.925. The heavier varieties, 0.925 to 0.940, are not so desirable for paint or varnish purposes, owing to their less pleasant odor and comparatively slight volatility.

125. Correct designation. The name "pine oil" as applied to these terpenes is, in the opinion of the author,

somewhat of a misnomer, and a name like "heavy turpentine" is much more applicable, as these bodies very closely resemble the ordinary turpentine in their properties and show little analogy to the fixed or non-volatile oils, or to the rosin oil, except those fractions having a gravity of upwards of 0.940.

126. Properties. A desirable "heavy turpentine" is completely volatile, without leaving an oily stain, in about 6 hours, when 3 drops are allowed to fall on the same spot on a sheet of ordinary filter paper. When used with linseed oil such a turpentine acts as a true drier, and in this respect is even superior to ordinary turpentine. As its rate of evaporation from the oil or paint film is much slower, its effect is exerted for a much greater length of time. This can readily be demonstrated by placing on a sheet of glass some raw linseed oil, a mixture of 90 parts of linseed oil to 10 of turpentine, and 90 parts of linseed oil to 10 of heavy turpentine; then placing the sheet of glass at an angle of about 30 degrees from the perpendicular and noting the rate of drying. For ready mixed paints for outside use and for liquid driers for the store and manufacturing trades, the heavy turpentines offer great possibilities, as these turpentines can be obtained for from 10 to 15 cents below gum turpentine, and by reason of their great drying strength permit the use of considerable quantities of naphtha for thinning to suitable consistency.

127. Value as a drier. It is quite generally conceded that one of the causes of the ultimate breaking down of linseed-oil paints is the fact that the metallic driers used to hasten the drying of the linseed oil do not cease their action on accomplishing the drying of the paint film, but continue their oxidizing action, slowly

but nevertheless surely, converting the dry but elastic oil film, or linoxyn, into a brittle, non-elastic substance, which, having lost its life or binding strength, readily crumbles and disintegrates. The greater the extent to which metallic driers can be avoided and yet secure proper drying of the paint, the longer the life of the paint. A drier composed of naphtha, heavy turpentine, and a small quantity of resinate or linoleate drier affords a product much superior to the medium or low-priced driers on the market. The same reasons hold good for the use of the heavy turpentines in outside mixed paints.

128. Use in varnishes. In quick-drying varnish products and paints the use of a drier is not advantageous except in special cases. It is possible to make extremely short oil varnishes, 6 to 7 gallons of oil per 100 lbs. of gum, by starting the thinning at 450° F. to 480° F. with a heavy turpentine of specific gravity of about 0.910, using about 2 gallons or just a sufficient amount to reduce the temperature of the kettle to the point of safety for the addition of turpentine or petroleum spirits for the completion of the thinning. If added promptly it will save a kettle of varnish that has begun to curdle in the initial stage of thinning from lack of sufficient heat or other causes.

129. Standard of purity. As before stated, the heavy turpentines should be selected with regard to freedom from material percentages of fractions heavier than 0.930. Also, as some of the largest producers of these oils obtain their products with the aid of a petroleum solvent, the presence of mineral oils must be looked for, which if present in quantity will leave a greasy stain on paper. As the boiling point of a heavy turpentine will be between 190° C. and 225° C., distillation with direct heat

will cause a certain amount of decomposition, especially of the heavier fractions, and distillation at 100° C. with steam through a LeBel-Henninger column results in a very slow distillation, about 15 c.c. of turpentine to 85 c.c. of water. It will be found advisable to heat the distilling flask in a paraffine oil bath to 160° C., and while maintaining this temperature with care, pass a current of steam through the heated turpentine, distill, and examine the fractions as above outlined with special reference to the index of refraction.

Polymerization with sulphuric acid does not yield satisfactory results, as a considerable percentage remains unacted upon.

CHAPTER IX.

TURPENTINE SUBSTITUTES.

130. Use of volatile petroleum thinners. A word may be said in connection with the increased use of volatile petroleum products as paint thinners. In discussing this subject a prominent paint chemist states the problem as follows:

"The rapid depletion of our turpentine forests and the rapid advance in the price of turpentine has brought prominently before every paint and varnish manufacturer the absolute necessity for some volatile solvent capable of replacing entirely or in part the turpentine he used." The answer to this problem has been, naturally, the flooding of the market with an innumerable number of substitutes of uncertain merit. Some of the smaller paint companies, and especially those making paint for "a price," have adopted some of these substitutes without a careful investigation of their merits. On the other hand, some of the larger and more completely equipped companies have devoted considerable study to the question of turpentine substitutes, first endeavoring to ascertain the exact function of the turpentine in the paint and then seeking to prepare an article that would have the same essential properties and at the same time be free from objectionable characteristics.

131. Function of turpentine. According to the views of leading chemists the purpose of the turpentine in the paint is to increase the penetration of the oil and pigments into the wood and the undercoats of paints;

to produce a "flat" or "semi-flat" surface, permitting a closer union with the succeeding coat, or for appearance, as in the case of paints intended for inside use; to render the paint more fluid without the use of an excessive amount of oil; to increase the speed of the drying of the paint both by evaporation and by oxidization; and finally, to act as a bleaching agent on the oil, rendering the paint whiter; this, however, is not so essential as the other functions of the turpentine. Naturally chemists turned to the various petroleum products in their search for the desired substitutes, and as a result of their studies a number of companies are using a product which does not behave like any of the petroleum distillates with which the chemist is ordinarily familiar.

132. **Characteristics.** This product is used under various trade names and differs slightly in composition, according to the petroleum or petroleums from which it is derived, i.e., whether of Texas, Russian, or of some other origin. It is prepared so that it has a flash point slightly above that of turpentine, and hence as a fire risk it is as safe as turpentine, which is in marked contradistinction to benzine. It evaporates cleanly, and at a rate about or slightly slower than ordinary turpentine. In securing penetration of the paint it is fully equal to turpentine and is free from objectionable odors. In order to overcome the deficiency of not assisting the paint in drying by oxidization and the lack of bleaching action on the linseed oil, several paint manufacturers add a sufficient percentage of spirits of turpentine to supply these desired qualities.

133. **Reporting results.** The chemist in making an analysis of paints should be very careful in stating the composition of the volatile oils used in the vehicle, and

should not confound these turpentine substitutes with ordinary benzine, which costs considerably less than half as much and is dangerous to use on account of the fire risk and is too volatile to be accepted as a proper turpentine substitute. The analysis of these substitutes when once incorporated into the paint is somewhat difficult, but with care may be obtained by distillation, as above mentioned. Having secured the volatile distillate and having freed it from all traces of water, it may be redistilled, using a small distilling flask and carefully noting the temperatures at which the product passes over. The substitutes of recognized merit distill usually between 150° and 200° C. Any benzine present will pass over below 150° C., and kerosene mostly above 200° C. If the latter is present, however, a large portion will not be volatile in the steam distillation and will remain in the linseed oil, being readily detected in the latter by pouring six drops in a few cubic centimeters of an alcoholic solution of potash, boiling gently for two minutes, and pouring into a little distilled water, a decided cloudiness indicating the presence of unsaponifiable petroleum oils.

134. **Analyses.** The following data clearly indicate the characteristics of the petroleum products which are now being offered in large quantities as satisfactory in whole or in part for spirits of turpentine:

ANALYSIS OF DIAMOND T SPIRITS.

Specific Gravity, 0.8185 — 41.38° Beaumé.
Flash Test, 96° F. (open) — 35.56° C.

DISTILLATION BY TEMPERATURES.

	C.	C.
Commencing at	151.67	
From	151.67	to 157.23 — 10%
Do.	157.23	to 162.78 — 17%
Do.	162.78	to 168.34 — 28%
Do.	168.34	to 173.89 — 38%
Do.	173.89	to 179.45 — 47%
Do.	179.45	to 185.00 — 56%
Do.	185.00	to 190.56 — 65%
Do.	190.56	to 196.11 — 71%
Do.	196.11	to 201.67 — 76%
Do.	201.67	to 207.23 — 80%
Do.	207.23	to 212.78 — 85%
Do.	212.78	to 218.34 — 88%
Do.	218.34	to 223.89 — 91%
Do.	223.89	to 229.45 — 93%
Do.	229.45	to 235.00 — 94%
Do.	235.00	to 240.56 — 95%
Do.	240.56	to 246.11 — 97%
Do.	246.11	to 248.89 — 98%

Name of Material.	Texene.	Turpentine.	P. Naphtha.
	Per cent.	Per cent.	Per cent.
Sulphur	.008	.003	.003
Solubility of white lead in	.000	.002	.001
Non-vol. solids at 212° F.	.022	.510	.050
Discoloration of outside paint	None	None	None
Discoloration of inside paint	None	None	None
Amount of paint vehicle separated from paint after six days:			
In outside paint	18.2	15.7	19.8
In inside paint	18.4	12.1	20.0
Loss in 3 hrs. at room temp.	20.6	15.5	74.5
Do. 24 do.	39.8	33.6	99.7
Do. 48 do.	65.7	55.6	Comp.
Do. 72 do.	76.7	91.6	Comp.
Do. 96 do.	95.3	Comp.	Comp.
Do. 120 do.	99.4	Comp.	Comp.
Evaporation completed in approx.	5 days	4 days	1 day
Solubility in linseed oil	Complete in all proportions.		

DISTILLATION FIGURES OF TEXENE, TURPENTINE, AND NAPHTHA.

			Texene.	Turpentine.	Naphtha.
1st.	10%	distilled bet. deg. Fahr.	300–307	307–315	169–208
2d.	10%	Do.	307–313	315–316	208–216
3d.	105%	Do.	313–322	316–318	216–221
4th.	105%	Do.	322–338	318–318	221–226
5th.	10%	Do.	338–351	318–318	226–235
6th.	10%	Do.	351–361	318–318	235–243
7th	10%	Do.	361–372	318–318	243–252
8th.	10%	Do.	372–390	318–320	252–266
9th.	10%	Do.	390–417	320–325	266–291
10th.	10%	Do.	417–441	325–338	291–313

135. Distillation with steam through a LeBel-Henninger column, as described in the preceding chapter, with the Sun Oil Company's No. 18 Oil, which is a well-known petroleum substitute, gave the following results:

PETROLEUM SPIRITS.

Flash Point, 92° F. (Open). Distillation, 145° C. – 225° C.
Time Distillation, P.S., 74 m. 304 c.c.

	Comb. Distillate.	Water.	Petroleum Spirits.	Temperature.	Time.
	c.c.	c.c.	c.c.	Deg. C.	m.
1	100	42	58	95	6
2	100	50	50	96	7
3	100	58	42	97	7
4	100	64	36	98	8
5	100	71	29	98	8
6	100	77	23	98	8
7	100	81	19	98	8
8	100	84	16	98	8
9	100	88	12	98	8
10	100	89	11	98	8

Residue 8

CHAPTER X.

THE INERT PIGMENTS.

136. Classification. The inert pigments comprise

Barium sulphate (barytes, blanc fixé).
Barium carbonate.
Calcium carbonate (whiting, Paris white, white mineral primer).
Calcium sulphate (gypsum, terra alba).
China clay (kaolin).
Asbestine (magnesium silicate).
Silica (silex).

The properties of the various active pigments have been discussed under their methods of manufacture and need not be taken up here.

137. Inert pigments. The inert pigments have widely different properties, not only from a chemical standpoint but from a physical standpoint as well; and while two pigments may have the same chemical composition, they may differ greatly in physical properties, producing entirely different results when used in paints. Hence it is practically impossible from the chemical analysis to judge the service values of paints containing inert pigments. Chemical analysis, however, in conjunction with a careful microscopic examination, especially if a polarizing microscope be used, may give some idea of what the service value should be.

138. Barium sulphate (barytes, blanc fixé). Barytes is perhaps the most extensively used of the inert pigments. It more nearly approximates white lead in specific grav-

ity and oil-taking capacity than any of the others. It is absolutely unaffected by acids, alkalies, or atmospheric influences of any kind. Its hiding power or opacity when ground in oil is very low, and hence when used in any considerable percentage in a mixed paint or combination lead its presence is indicated by the reduced opacity of the paint film. The requisites of a high grade of barytes are whiteness and fineness. Commercial grades often contain varying percentages of calcium carbonate, which will be indicated by effervescence when treated with hydrochloric acid. Occasionally a considerable percentage of calcium sulphate may be found which may be readily estimated by extracting with boiling water and determining the calcium in the filtrate.

During the past few years numerous new barytes deposits have been opened up and in some instances have afforded a product of doubtful value to the paint manufacturer, due to a lack of proper grinding and a peculiar crystalline structure which gives much trouble in the paint mixer and grinding mill and causes excessive settling in the package. In fact it is always advisable for the chemist to have his report confirmed by trying out the product in question in one or more regular formulas in the factory. Neither is the color maker immune from trouble with his barytes, especially in the manufacture of chrome greens, resulting in excessive settling of his green in mixed paints and manufacturing trades paints, especially dipping paints. The cheaper grades of barytes have a yellowish gray color and are often treated with sulphuric acid to improve the color by removing the iron. A considerable portion of the barytes on the market is "blued," either by precipitating as Prussian blue, the iron sulphate obtained by

the treatment with sulphuric acid or by adding the Prussian or ultramarine blue separately. The majority of paint manufacturers, however, prefer to blue their goods themselves, if necessary, during the process of manufacture. The fineness with which barytes has been ground can easily be determined by examination under the microscope after the acid soluble pigments have been dissolved out.

139. **Free acid.** Each shipment of barytes should be carefully examined for free acid, which can be easily done by placing a sample on a strip of litmus paper in a watch glass and moistening with a little distilled water. The degree of reddening will indicate whether more than a minute trace of free acid is present. In case of doubt, a quantitative determination should be made. The presence of free sulphuric acid, especially in the case of a combination lead ground in a warm mill, will cause a decided hardening in the keg. Also if an acid barytes be ground with lithopone the offensive odor of hydrogen sulphide will be very apparent, not only in the grinding room but when the package is subsequently opened.

140. **Blanc fixé.** This pigment is a precipitated barium sulphate. Owing to its more amorphous character it has a much greater hiding power than barytes. Its oil-taking capacity is greater; it does not settle in a paint so badly as barytes and is much whiter; its cost, however, is about twice as great. It is largely used as an inert base for organic lakes.

141. **Barium carbonate.** This pigment is used comparatively little in the United States as a paint pigment. In physical and chemical properties it much resembles white mineral primer, a form of calcium carbonate, although it does not require so much oil in grinding.

Its specific gravity is about that of barytes. It dissolves readily in acetic, nitric, and hydrochloric acids; sulphuric acid converts it slowly into insoluble barium sulphate. In the hundreds of mixed paints examined by the writer barium carbonate was found to be present in only one paint, although its presence in certain organic lakes, especially in certain shades of red, is not uncommon in a precipitated form.

142. Calcium carbonate, Paris white, whiting, alba whiting, white mineral primer.

Under the heading of *calcium carbonate* we have three distinct classes of pigments, — those obtained from

(1) English cliffstone or similar chalk formations, such as Paris white, gilders' whiting, and commercial whiting.

(2) Marble or a crystalline calcium carbonate, such as marble dust, white mineral primer, etc.

(3) Precipitated calcium carbonate, such as alba whiting.

The English cliffstone pigments are usually put on the market in about three grades. The first grade is the whitest and most finely ground and bolted and is usually sold under some such name as *Paris white*, and finds its use largely in first-quality mixed paints and combination leads. The second grade is coarser and has a slightly grayish tint and is usually sold under some such name as *gilders' whiting*. It is also bolted, and is used in second and third grade paints. The third grade is inferior in color and fineness to the other two grades. It finds its chief use in kalsomine; although it is used in some of the very inferior paints, it never should be, owing to the fact that it

is not bolted, and therefore contains some relatively large particles. It is usually sold as commercial whiting.

143. White mineral primer. The various forms of white mineral primer are of an entirely different nature physically from the cliffstone products, being fragments of small crystals. They have very little body in oil, being nearly transparent. They are usually whiter than Paris white and possess much greater tooth, but are not much used in mixed paints owing to the fact that they settle badly in the can and have very little opacity. They find their chief use in primers and in putty for making it work shorter. Being of a crystalline nature it is natural that they require less oil in grinding than Paris white.

Alba whiting and other precipitated calcium carbonate pigments are very white, but being very light and fluffy require an enormous amount of oil in grinding.

While it is not an easy matter to distinguish these different products in a paint, yet the microscope is of much value in determining the fineness of grinding.

The paint chemist is frequently required to pass on samples of Paris white, which appear much whiter than his standard samples. On close examination these will usually be found to possess a semicrystalline nature, therefore are deficient in opacity, and are not true Paris whites.

Quantitative Analysis of the Calcium Carbonate Pigment.

144. **Moisture.** Heat 2 grams at 105° C. for two hours, cool, and weigh.

145. **Silica.** Weigh one-half gram into a suitable sized casserole. Cover, add 5 c.c. of hydrochloric acid (sp. gr. 1.1) by means of a pipette, without raising the cover. After the effervescence has ceased, rinse off the beaker cover with a little hot water. Evaporate to dryness and cool. Add 2 c.c. of concentrated hydrochloric acid, again evaporate, and heat gently for a few minutes. Cool and dissolve in 100 c.c. of hot water and 10 c.c. of strong hydrochloric acid, filter, wash, ignite, and weigh. If 1 per cent or under, it may be regarded as silica. If more, it should be fused with sodium carbonate, dissolved in water and hydrochloric acid, in the same casserole, and evaporated to dryness. Heat gently. Add a little more hydrochloric acid and dehydrate again. Finally take up in water acidulated with hydrochloric acid, filter, ignite, and weigh as silica. The filtrate from the silica fusion is treated as described under 149.

146. **Alumina and iron.** The filtrate from the original residue is made just perceptibly alkaline with dilute ammonia, the iron and alumina filtered off, ignited, and weighed in the usual manner.

147. **Calcium.** The filtrate from the iron and alumina is made acid with acetic acid, boiled, and 40 c.c. to 50 c.c. of ammonium oxalate solution added. Continue boiling for 5 minutes, filter, and wash thoroughly. Return filter and precipitate to same beaker. Add 200 c.c. of boiling water and 25 c.c. of dilute sulphuric acid and

titrate with standard tenth-normal potassium permanganate.

1 c.c. tenth-normal permanganate	= 0.0028 g. CaO
1 c.c. tenth-normal permanganate	= 0.0050 g. $CaCO_3$
1 c.c. tenth-normal permanganate	= 0.0086 g. $CaSO_4 . 2H_2O$
1 c.c. tenth-normal permanganate	= 0.0068 g. $CaSO_4$
1 c.c. tenth-normal oxalic acid	= 0.0028 CaO
Cryst. oxalic acid × 0.444	= CaO

EXAMPLE: Wt. sample taken	= 0.250 g.
Titration with permanganate	= 50.5 c.c.
25 c.c. standard iron solution	= 31.8 c.c. permanganate
1 c.c. standard iron solution	= .007 g. iron
1 c.c. tenth-normal iron solution	= .0056 g. iron
25 c.c. standard iron solution	= 31.25 c.c. tenth-normal permanganate.
1 c.c. permanganate solution used	= 0.983 c.c. tenth-normal permanganate.
50.5 c.c. × 0.983	= 4964 c.c.
(49.64 c.c. × 0.0050) ÷ 0.250	= 99.28% $CaCO_3$.

148. Magnesium. The filtrate from the calcium oxalate is cooled and treated with hydrogen sodium phosphate, allowed to stand for one-half hour, then 25 c.c. of strong ammonia added, allowed to stand one hour, filtered on a Gooch crucible, ignited, and weighed.

Wt. precipitate = 0.7575 = Wt. Magnesium carbonate.

149. Calcium and magnesium oxides. The filtrate from the silica fusion should be treated separately from the main filtrate, as the calcium and magnesium obtained from it are to be reported as oxides and not as carbonates. Precipitate the iron and alumina, calcium and magnesium, as described under 146, 147, and 148.

NOTE. — If the sample contains considerable magnesium carbonate, the following modification should be observed. After filtering off the iron and aluminium hydroxides, they are redissolved in another beaker, diluted, and again precipitated and filtered into the main filtrate. The

same treatment is given to the calcium oxalate. Magnesium compounds when present in considerable percentages badly contaminate the other precipitates.

150. ANALYSES OF CALCIUM AND MAGNESIUM CARBONATE PIGMENTS BY AUTHOR.

	I. White Ocher.	II. Whiting.	III. English Cliffstone.	IV. Magnesite.
Moisture	0.11	0.30	1.60	0.07
Silica	1.21	0.90	2.02	2.04
Iron oxide and alumina	.63	0.20	1.00	3.01
Calcium carbonate	97.39	96.55	92.81	10.84
Magnesium carbonate	0.56	1.84	2.52	83.91
Undetermined	0.10	0.21	0.05	0.13
	100.00	100.00	100.00	100.00

151. **Calcium sulphate (gypsum, terra alba).** This pigment is found in combination white leads and exterior white paints only to a limited extent. Its chief use seems to be in certain lines of railroad paints and in dipping or implement paints. It is also used to some extent as a base upon which to strike certain organic lakes, notably the para reds. The writer, despite the favorable opinions of many eminent paint authorities, does not believe that calcium sulphate, or gypsum, as it is more commonly known, is adapted for use in exterior paints owing to its solubility in water, it being soluble about one part in five hundred. A linseed oil paint film is by no means impervious to moisture, and the continued action of rains and storms cannot be otherwise than favorable, as the solvent action of the water in removing a portion of the gypsum renders the paint film more porous and its disintegration more rapid.

152. **Calcium sulphate in oxide of iron pigments.** Venetian reds often contain 50 to 80 per cent of calcium sulphate. The better class of Venetian reds are

composed of 50 per cent of ferric oxide and 50 per cent of calcium sulphate. This calcium sulphate should not be confounded with the forms above discussed, as it has been subjected to the action of a high heat and is therefore insoluble in water, and is regarded as a proper constituent of Venetian reds.

153. **Analysis of agalite, terra alba, etc.** These pigments have essentially the same composition — calcium sulphate plus 2 molecules of water. The same method of analysis may be pursued as described under the analysis of calcium carbonate pigments. In addition, it is necessary to determine the combined water by ignition to constant weight, and also to determine the combined sulphuric acid, which may be done as follows:

Boil 0.5 gram of the pigment in 30 c.c. of strong hydrochloric acid for 10 minutes in a covered beaker. Dilute with 250 c.c. of boiling water, boil 5 minutes, filter, make filtrate neutral with ammonia, then distinctly acid with hydrochloric acid, and bring to boiling. Add 25 c.c. of barium chloride, boil 10 minutes, filter, wash with hot water, ignite, and weigh.

Wt. barium sulphate $\times$ 0.3433 = combined sulphuric acid.

154. ANALYSES OF CALCIUM SULPHATE PIGMENTS BY AUTHOR.

	I. Agalite.	II. Terra Alba.
Moisture and combined water	19.02	20.67
Iron oxide and alumina	0.29	0.67
Silica	5.60	0.70
Calcium sulphate	74.90	76.52
Magnesium sulphate	.....	1.36
Undetermined	0.19	.08
	100.00	100.00

155. Aluminum silicate (China clay, kaolin, tolanite). This pigment also finds but little use in combination white leads, owing to its low specific gravity. It is, however, used extensively in mixed paints, implement paints, and as an inert base upon which to strike para and other organic reds, especially for colors which are used in dipping paints. Its functions and properties are very similar to those of magnesium silicate, it being essentially a suspender for preventing settling in paints. It is very inert in its action with acids and alkalies. Strong hydrochloric acid with continued boiling will dissolve a very slight fraction of 1 per cent, hence traces of aluminum may be found in a hydrochloric acid solution of a paint containing aluminum silicate. Some of the silicates much in favor with the paint trade contain a considerable percentage of what is apparently uncombined silica. In mixed paint it is often used with magnesium silicate. Hence a microscopic examination is usually required to determine whether the latter is present or not. It yields to treatment by fusion with sodium carbonate more readily than magnesium silicate. When subjected to a high temperature it loses 11 to 13 per cent of water of hydration.

156. Magnesium silicate (asbestine pulp, talcose). This pigment is sold under the various names of white silicate, asbestine, asbestine pulp, etc. Large amounts are obtained from natural deposits in and around Gouverneur, N. Y. It has a very low specific gravity, and is much used in lead and zinc paints to prevent those pigments from settling hard in the bottom of the package. Chemically it is very inert, being unacted upon by any of the ordinary acids. It is, however, decomposable with hydrofluoric acid in a platinum dish

and by fusion with sodium carbonate. Fusion with potassium bisulphate decomposes it only partially. Continued heating at a bright red heat will cause a loss of 3 to 5 per cent in weight, due to loss of water of hydration. It is easily recognized under the microscope by the fibrous or rod-like structure of the particles.

157. Silica (silex). There are two distinct kinds of silica to be found on the market, — that obtained from crushed quartz, which is a very pure form of silica, and an impure form found in natural deposits, especially in Illinois. The former possesses a very pronounced "tooth," under the microscope the particles are very sharp and jagged, and it is quite transparent in oil. The second form is composed of rounded particles of a complex chemical nature; besides free silica there are usually found associated with it calcium carbonate, aluminum silicate, and magnesium silicate, besides a small amount of magnesium carbonate. This product requires more oil in grinding, and has much more body, but considerably less tooth.

158. Fusion with sodium carbonate. One-half gram is thoroughly mixed with 10 grams sodium carbonate and one-half gram potassium nitrate placed in a covered platinum crucible and fused until quite clear and quiet. Cool, and dissolve in water in a casserole, provided with beaker cover, on the hot plate. Make acid with hydrochloric acid, adding the acid with a pipette, keeping the casserole covered to avoid loss. Also rinse out the crucible with a little acid. After the effervescence is over, wash off the watch glass, and evaporate to dryness on the sand bath. Cool, moisten residue with hydrochloric acid, and evaporate to complete dryness again. Dissolve in 10 c.c. of hot water and 10 c.c. of hydro-

chloric acid. Filter, ignite, and weigh precipitate as silica.

If barytes is suspected to be present, the sodium carbonate fusion is dissolved in hot water and the barium carbonate filtered off, dissolved in hydrochloric acid, and precipitated with a few drops of sulphuric acid in the usual manner. The filtrate from the barium sulphate is added cautiously to the filtrate from the barium carbonate, the mixed filtrate made acid, and the silica dehydrated as described above.

159. The filtrate from the silica is made slightly alkaline with ammonia and the iron and alumina precipitated, washed, redissolved, reprecipitated to free from sodium salts, filtered, ignited, and weighed in the usual manner.

The filtrate from the iron and alumina is treated with ammonium oxalate and after allowing to stand in a warm place the calcium is filtered off, ignited, and weighed as calcium oxide. If desired the calcium may be estimated volumetrically, as described under the analysis of white mineral primers, etc.

The filtrate from the calcium is tested for magnesium with sodium hydrogen phosphate, and if found, estimated in the usual manner.

The carbon dioxide is determined in a separate portion of the sample. The amount found is combined with the requisite amount of calcium to form calcium carbonate. Any excess of calcium is reported as the oxide, it being in combination with the silica. The magnesium is usually calculated as magnesium oxide, unless the carbon dioxide is in excess of the calcium present, in which case it is calculated to magnesium carbonate and the remainder of the magnesium to the oxide.

160. Moisture. Heat 2 grams at 105° C. for 3 hours, cool, and weigh.

161. Combined water. Weigh 2 grams into a platinum crucible, heat in the muffle or over a strong Bunsen flame for 1 hour. Loss in weight equals combined water unless an appreciable amount of carbonate is present.

162. Determination of the alkali metals, sodium and potassium. Heat gently 1 gram of the sample intimately mixed with 1 part ammonium chloride to 8 parts of pure calcium carbonate. The alkalies as well as some of the calcium are converted into chlorides. Cool, treat with water. The alkali chlorides will dissolve, while most of the calcium remains undissolved. Filter, precipitate the calcium with ammonia and ammonium carbonate, filter, evaporate to small bulk, and precipitate any remaining calcium. Filter. The solution now contains as fixed compounds only sodium and potassium chlorides. Evaporate nearly to dryness in a weighed platinum dish on water bath. Cover and dry completely on the hot plate, exercising great care to prevent the spattering of the material. Finally heat gently with a Bunsen burner, which must be held in the hand and the flame waved under the dish and removed as soon as any portion of the dish becomes red hot. Cool and weigh. Take up in water and add an excess of platino-chloride solution. Evaporate to a sirupy consistency, take up with 80 per cent alcohol, filter through a weighed Gooch crucible, and wash with alcohol. Dry in the steam oven.

Wt. of precipitate $\times$ 0.1941 = wt. Potassium oxide.

Calculate to potassium chloride, subtract from the weight of the mixed chlorides, thus obtaining the weight of sodium chloride, which may then be calculated to sodium oxide.

163. ANALYSES OF SILICAS BY AUTHOR.

	I.	II.	III.
Moisture	0.21	0.06	0.43
Ferric oxide and alumina	0.28	0.01	1.48
Silica	99.40	99.88	53.48
Calcium carbonate	.....	.....	26.12
Magnesium carbonate	.....	.....	18.17
Undetermined	0.11	0.05	0.32
	100.00	100.00	100.00

ANALYSES OF MAGNESIUM SILICATES BY AUTHOR.

	I.	II.
Moisture	0.50	0.29
Combined water	2.99	3.44
Silica	58.60	56.76
Ferric oxide	0.09	0.18
Alumina	1.43	2.84
Calcium carbonate	.....	2.77
Calcium oxide	5.63	.....
Magnesium oxide	30.45	33.50
Undetermined	0.31	0.22
	100.00	100.00

ANALYSES OF TOLANITE BY AUTHOR.

Moisture	0.22
Combined water	10.42
Ferric oxide	0.09
Alumina sol. in HCl	0.39
Silica	65.51
Alumina	23.12
Undetermined	0.25
	100.00

TYPICAL ANALYSES OF CLAYS.[1]

	I.	II.	III.	IV.
Silica	45.45	66.20	72.66	64.84
Alumina	38.75	24.11	17.33	24.31
Ferric oxide	1.15	0.79	1.05	1.60
Calcium oxide	.....	.....	0.13	0.11
Magnesium oxide	0.11	.....	.....	.....
Potassium oxide	0.17	0.96	0.36	0.24
Sodium oxide	.....	.....	0.38	0.32
Combined water, etc.	13.05	7.20	8.09	8.58
Undetermined	1.32	0.74	.....	.....
	100.00	100.00	100.00	100.00

[1] Geological Survey of North Dakota, 1901.

164. Specifications for paste wood filler. ("Bureau of Supplies and Accounts, Navy Department," 1902.) Paste wood filler shall contain the following:

	Per cent.
Silicate	65
Raw linseed oil	10
Best quality rubbing varnish	25

The silicate must be dry, finely ground, and when subjected to microscopic test the particles must show a needle-pointed shape. Powdered silicate which shows spherical fragments will not be accepted.

The raw linseed oil must be absolutely pure, well-settled oil, of the best quality; must be perfectly clear, and not show a loss of over 2 per cent when heated to 212° F. or show any deposit of foots after being heated to that temperature. The specific gravity must be between 0.932 and 0.957 at 60° F.

The rubbing varnish to be of the best quality and to be equal in quality to the standards of rubbing varnish, which can be seen on application to the general storekeeper's office at the various navy yards. Any indication of the use of rosin or any other adulterant in this varnish will be sufficient for its rejection.

The paste wood filler when thinned with turpentine to a brushing consistency must dry hard on glass in 24 hours. It must not rub up by friction under the finger, and when immersed in water must remain intact for at least 4 hours. It must dry full without luster, and be transparent, so that it will not color or cloud the work, and be hard enough to stand sandpaper without clogging the paper after 12 hours.

CHAPTER XI.

ANALYSIS OF WHITE LEAD.

165. Color. The two samples are weighed out in gram lots on a large glass plate, twelve drops of bleached linseed oil added to each and rubbed up thoroughly, and matched up on a microscope slide, the color being judged from both sides of the glass. After comparing the color, place the slide in the steam oven for two hours. This will give some idea as to the amount of yellowing that will occur when the lead is used in painting. This defect is particularly marked in pulp leads.

166. Opacity. Two grams each of the sample and standard are very carefully rubbed up with .01 gram of ultramarine blue and twenty-four drops of oil as described under the section on the "Determination of the tinting strength of colors." The more strongly the lead is colored, the weaker it is in hiding power or opacity. Adding weighed amounts of lead until the colors are of equal depth will show the ratio between the two.

167. Painting test. The painting value is best judged by painting test boards, as described under the section on the "Comparison of paints for covering power," and afterwards exposing them under suitable conditions.

168. Sulphur dioxide. In the manufacture of quick-process white leads, where the carbon dioxide is obtained from fuel gases, it is liable to contain sulphur compounds which will remain in the white lead combined in the form of sulphite of lead.

169. The sulphur dioxide may be estimated by treating 10 grams of the pigment with 50 c.c. of water and

25 c.c. of hydrochloric acid. Allow to stand 5 minutes and titrate with a hundredth normal iodine solution as described under the estimation of sulphur dioxide in zinc pigments. The same objections apply to its presence in white lead as in zinc oxides.

170. Sandy lead.[1] "A certain degree of density is always desired in white lead, since both the corroder and the grinder know that the smaller the amount of oil required to bring a given lead to paste form, the cheaper it is for him, since the average price per pound of linseed oil is greater than that of dry lead, while the same pigment is equally sought after by the consumer, since he, too, desires density and opacity in this pigment. However, efforts in this direction are not infrequently carried too far, with the result of a crystalline overcorroded lead which settles and hardens badly. Such lead causes loss and trouble both to the grinder and the consumer."

171. Determination. "Based upon the undesirable feature of settling, a comparative separation is easily made. A fairly large sample, say 100 grams, is taken. This, if in paste form, is thinned with benzine and run through a fine bolting cloth. Any paint skins are retained, but all of the lead should, when sufficiently thinned, wash through a fine bolting cloth. The very thin paint is now thoroughly stirred and allowed to settle for only a short time. Nearly all of the benzine is now poured off and then the washing of the sediment with benzine is repeated until the benzine comes off nearly clear, leaving the 'sand' alone as a residue." While present in all commercial lead, the amount should be small, scarcely exceeding 2.5 per cent; objectionable samples will frequently show much more, at times over 10 per cent.

[1] Hooker, Treatise on White Lead, page 24.

172. **Tanbark.** The determination of tanbark and other organic matter is seldom required. It may, however, be made by dissolving 50 grams of the sample in 75 c.c. of nitric acid diluted with 250 c.c. of water. Filter through a weighed Gooch crucible, provided with a disk of filter paper on the top of the asbestos felt, wash thoroughly, dry, and weigh. The amount present should not exceed one-tenth of one per cent, according to Hooker.

173. Sulphate of lead, which may be present in some of the quick-process leads, would largely remain undissolved in the nitric acid solution and unless removed would be weighed up as tanbark, etc. When present it may be dissolved by placing the Gooch crucible and contents in a small beaker containing acid ammonium acetate for a few minutes, after which the crucible is placed in the holder, washed with a further quantity of acetate solution, then with a little warm water, and dried as before.

174. **Metallic lead.** Like the determination of sandy lead it is seldom made. Occasionally in poorly prepared white leads a sufficient amount may be present to warrant a determination, in which case it is best made in conjunction with the determination of "sandy lead," which, after being weighed up, is carefully dissolved in dilute nitric acid, the operation being checked the moment the sandy white lead has dissolved by dilution with a large quantity of water. The particles of metallic lead are but very slightly acted upon by acid and may be filtered off on a weighed Gooch crucible, washed thoroughly, dried, and weighed. The amount found should not exceed one-tenth of 1 per cent.

175. **Lead sulphate.** This impurity may be present in small quantities in white leads prepared by the newer

processes and sometimes in old Dutch process lead in the settling tanks and wash-water tanks. When present in quantities less than one-half of 1 per cent it should not be considered as seriously objectionable.

176. **Determination.** Dissolve 1 gram in water 25 c.c., ammonia 10 c.c., hydrochloric acid in slight excess. Dilute to 200 c.c., and add a piece of aluminum foil which should about cover the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, boil until the bromine is expelled, add 15 c.c. of barium chloride, boil 10 minutes, filter, wash with hot water, ignite, and weigh as barium sulphate. Calculate to lead sulphate by multiplying by 1.3 as a factor.

177. **Volumetric estimation of lead, Method I.**[1] Dissolve 1 gram in 15 c.c. nitric acid, specific gravity 1.20, neutralize the solution with ammonia in excess, and then make strongly acid with acetic acid. It is then boiled and standard potassium bichromate solution is run in from a burette in sufficient quantity to precipitate nearly all the lead. The liquid is boiled until the precipitate becomes orange colored. The titration is continued, one-half cubic centimeter or so at a time, the solution being well stirred after each addition of bichromate until the reaction is almost complete, which can be observed by the sudden clearing up of the solution, the lead chromate settling promptly to the bottom of the beaker; this will usually occur within 1 c.c. of the end of the reaction. The titration is then finished, the

[1] Wainwright, J. Am. Chem. Soc., Vol. XIX, page 389.

end point being indicated by the use of silver nitrate as an outside indicator, on a white plate.

The solution of the lead salt should be as concentrated as possible before titration and decidedly acid with acetic acid. The titration should be performed in a solution kept at all times as near the boiling point as possible.

178. Potassium bichromate solution. This should be of such strength that 1 c.c. equals approximately 0.01 gram of metallic lead, and should be standardized against a weighed amount of pure metallic lead as described above.

179. Silver nitrate solution. Dissolve 2.5 grams of silver nitrate in 100 c.c. of water.

NOTE. — This method is applicable for determination of lead in red lead, the solution being effected with nitric acid, boiling, and adding dilute oxalic acid drop by drop until the lead oxide formed is completly dissolved.

180. Volumetric estimation of lead, Method II.[1] Dissolve 0.5 to 1 gram of the pigment in acetic acid if white lead; if lead sulphide, dissolve in nitric acid, dilute with 25 c.c. cold water, add strong ammonia until just alkaline to litmus paper, then make distinctly acid with strong acetic acid.

181. Heat to boiling, dilute to about 200 c.c. with boiling hot water, and titrate with standard ammonium molybdate solution. Reserve about 10 c.c. of the hot solution in a small beaker, run in molybdate solution into the large beaker from a burette, with constant stirring, until a drop placed in contact with a drop of tannic acid solution on a white plate gives a brown or yellow tinge. Add the 10 c.c. reserved and finish the titration carefully at the rate of two drops addition at a time.

[1] Alexander's Method, Ore Analysis, Low, page 113.

When the final yellow tinge is obtained, it is probable that some of the immediately preceding test drops may have developed a tinge also. If such is the case deduct the volume of two drops from each test showing a color from the final burette reading.

182. Molybdate solution. Prepare a solution of ammonium molybdate 1 c.c. of which is equal to approximately .01 gram of lead. Standardize against a weighed amount of chemically pure lead, dissolving in nitric acid and treating as described above.

183. Tannic acid solution. Dissolve 0.5 gram of tannic acid in 100 c.c. of water.

184. Carbon dioxide. The amount of carbon dioxide in white lead can be most accurately estimated by means of Knorr's apparatus.

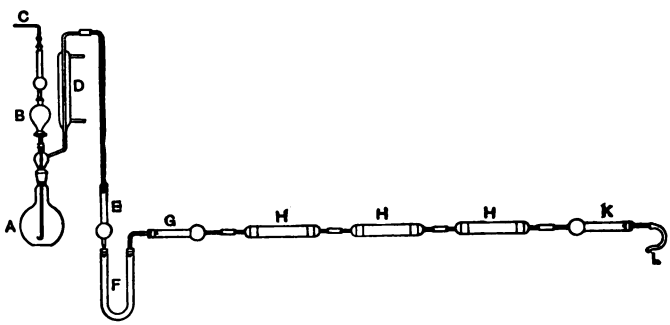

FIG. 5. — KNORR'S APPARATUS.

This apparatus employs only ground-glass joints, and may be quickly made ready for use or taken to pieces and packed away. On the other hand, it is inflexible and must be carefully handled. *A* is a distilling flask fitted to a condenser by a ground-glass stopper; *B*, reservoir containing acid; *C*, soda-lime tube; *D*, condenser; *E*, calcium chloride tube; *F*, U-tube filled with pumice

stone moistened with sulphuric acid, followed by a calcium-chloride tube *G*. The three soda-lime tubes *H*, *H*, *H* are followed by a calcium chloride tube *K*, which is connected with an aspirator at *L*.

The calcium chloride and soda lime employed should be finely granulated and freed from dust with a sieve.

185. One gram of the sample to be examined is placed in the distilling flask, which must be perfectly dry. The flask is closed with a stopper carrying the tube connecting with the absorption apparatus and also with the funnel tube. The tubes in which the carbon dioxide is to be absorbed are weighed and attached to the apparatus. In case two Liebig bulbs are employed, one for potassium hydroxide and the other for sulphuric acid, to absorb the moisture given up by the potassium hydroxide solution, it will be necessary to weigh them separately. If soda-lime tubes are employed it will be found advantageous to weigh them separately and fill the first tube anew when the second tube begins to increase in weight materially. The bulb *B* is nearly filled with hydrochloric acid (sp. gr. 1.1), and the guard tube *C* placed in position. The aspirator is now started at such a rate that the air passes through the Liebig bulbs at the rate of about two bubbles per second. The stopper of the funnel tube is opened and the acid allowed to run slowly into the flask, care being taken that the evolution of the gas shall be so gradual as not materially to increase the current through the Liebig bulb.

186. After the acid has all been introduced, the aspiration is continued, when the contents of the flask are gradually heated to boiling, the valve in tube *B* being closed. While the flask is being heated the aspirator tube may be removed, although many analysts prefer

when using ground-glass joints to aspirate during the entire operation. The boiling is continued for a few minutes after the water has begun to condense in *D*, when the flame is removed, the valve in the tube *B* opened, and the apparatus allowed to cool with continued aspiration. The absorption tubes are then removed and weighed, the increase in weight being due to carbon dioxide.

187. When extreme accuracy is desired the carbon dioxide after passing through the condenser should pass through a U-tube filled with calcium chloride, a U-tube filled with lumps of dehydrated copper sulphate moistened with sulphuric acid (sp. gr. 1.84), and then through a U-tube filled with pumice stone moistened with sulphuric acid before being absorbed by soda lime. The air used for aspirating should also pass through a large U-tube filled with soda lime before passing through the small soda-lime tube *C*. In order to make the apparatus compact the soda-lime tubes may be laid side by side on a small rack constructed for the purpose, the soda-lime tubes being connected with one another by small U-shaped glass tubing connections.

188. **Acetic acid in white lead.**[1] "In the manufacture of white lead by any process involving the use of acetic acid, a certain portion of the acetic acid seems to be bound firmly so that it cannot be washed out in any ordinary process of manufacture. The amount of the acetic acid which is fixed by the white lead depends largely upon the quantity used in the process of manufacture. The navy yard specifications demand a white lead which shall not contain 'acetate in excess of fifteen one-hundredths of 1 per cent of glacial acetic acid.' It seems reasonable, furthermore, that whether

[1] G. W. Thompson, J. Soc. Chem. Ind., Vol. XXIV, No. 9.

the acetic acid is objectionable or not, the intelligent purchaser of white lead should be enabled, as far as possible, to know what he is buying, and perhaps to trace back results to some definite cause."

189. "Ordinary lead acetate solution will take up varying amounts of lead oxide to form basic lead acetate. The more concentrated the lead acetate solution is, the less basic will be the formed acetate; for instance, the ordinary pharmacopœia solution — 'Liquor Plumbi Subacetatis' — contains two equivalents of lead to one of acetic acid, and, while this solution may be made more basic than this by adding an excess of litharge, the amount of litharge which it will take into solution in excess of that required to form the pharmacopœia solution is comparatively small."

190. "Working with dilute solutions of lead acetate, however, solutions can be obtained containing as much as ten equivalents of lead to one of acetic acid. These very basic dilute solutions may, however, be regarded by some as supersaturated solutions, for the reason that the basic lead tends to separate out on slight provocation, carrying with it some acetic acid. If this very basic lead acetate which separates out is washed with distilled water, it appears to form a colloidal solution from which the basic lead is readily precipitated in the presence of suspended inert material, and especially in the presence of electrolytes. Ordinary water is usually used for washing white lead, and, as this water contains more or less saline substances, any of this extremely basic acetate that is present will be precipitated with the white lead, and go into the finished product."

191. **Determination.** "18 grams of the dry white lead are placed in a 500-c.c. flask, this flask being arranged

for connection with a steam supply, and also with an ordinary Liebig condenser. To this white lead is added 40 c.c. of sirupy phosphoric acid, 18 grams of zinc dust, and about 50 c.c. of water. The flask containing the material is heated directly and distilled down to a small bulk. Then the steam is passed into the flask until it becomes about half full of condensed water, when the steam is shut off and the original flask heated directly and distilled down to the same small bulk, this operation being conducted twice. The distillate is then transferred to a special flask and 1 c.c. of sirupy phosphoric acid added to insure a slightly acid condition."

192. "The flask is then heated and distilled down to a small bulk — say 20 c.c. Steam is then passed through the flask until it contains about 200 c.c. of condensed water, when the steam is shut off and the flask heated directly. These operations of direct distillation and steam distillation are conducted until 10 c.c. of the distillate require but a drop of N/10 alkali to produce a change in the presence of phenolphthalein. Then the bulk of the distillate is titrated with N/10 sodium hydroxide, and the acetic acid calculated. It will be found very convenient in this titration, which amounts in some cases to from 600 to 700 c.c., to titrate the distillate when it reaches 200 c.c., and so continue titrating every 200 c.c. as it distills over.

193. **Conclusions.** "The details in this described method, as regards the supply of steam from an outside flask, its condensation and subsequent evaporation, are not essential to the process, but can, of course, be modified so as to conform to the ordinary method of distilling acetic acid from acetate of lime. If the white lead contains appreciable amounts of chlorine, it is well to add some silver phosphate to the second distillation

flask, and not to carry the distillation from this flask too far at any time. If the dry white lead under examination has been obtained by the extraction as a residue from white lead paste, it is well that this extraction should be exceedingly thorough, as otherwise fatty acids may be held and distilled with the acetic acid. Even then they will not interfere with the final titration, as they may be filtered from the distillate before titration, should that be desired."

194. ANALYSES OF MISCELLANEOUS WHITE LEADS MADE BY THE AUTHOR.

No.	Net Weight.	White Lead.	Lead Sulphate.	Zinc Oxide.	Barytes	Calcium Carbonate.	Silica.	Clay.	Undetermined.
I	13.5 oz.	9.98	.....	12.00	76.28	.....	1.10	.....	0.64
II	15.4 oz.	64.73	.....	3.60	30.43	.....	0.76	.....	0.48
III	14.8 oz.	4.69	.....	12.50	75.72	5.89	0.67	.....	0.53
IV	15.0 oz.	3.34	.....	8.96	72.35	4.52	.....	10.83	.....
V	.....	54.69	.....	17.38	25.57	.....	.....	.....	0.36
VI	1 lb., 14.2 oz.	.....	3.29	6.90	89.81	.....	.....	.....	.....
VII	1 lb., 14 oz.	10.69	.....	20.03	69.28	.....	.....	.....	.....
VIII	15 oz.	5.31	6.37	13.68	74.25	.....	.....	.....	0.39

None of the above products are entitled to be called white lead. Only one bore the name of the company putting out the product.

195. **Short weights of white lead packages.** All the white leads and so-called white leads, examined by the writer, have been found to be short weight. That is, the kegs supposed to contain 12½ pounds will actually contain, in each eight kegs which should have shown 100 pounds, only 83 to 89 pounds. As showing to what extent the different so-called white leads actually varied and fell short in weight, I give the following list:

Number.	Assumed Weight.	Net Weight.	
	Lbs.	Lbs.	Oz.
I	50	46	0
II	12½	11	13
III	12½	10	6
IV	12½	10	7
V	25	21	12
VI	25	22	7
VII	12½	10	0
VIII	12½	11	0

CHAPTER XII.

ANALYSIS OF SUBLIMED WHITE LEAD AND THE ZINC PIGMENTS.

196. The analysis of sublimed white lead.[1] *Lead and Zinc Oxide.* Weigh 1 gram into a small beaker, add 20 c.c. of 10 per cent sulphuric acid, stir well, and allow to stand 10 minutes, filter, and wash slightly with dilute sulphuric acid on filter.

Residue. Dissolve through filter with hot, slightly acid ammonium acetate solution, wash with hot water, and dilute to 200 c.c. with hot water. Add a slight excess of potassium bichromate solution and heat. Filter on Gooch crucible, wash with water. Dry, ignite, and weigh as lead chromate.

Filtrate. Add about 2 grams of ammonium chloride, heat to boiling, add excess of ammonia, and filter. Reject residue. Add 1 gram of microcosmic salt and a very slight excess of acetic acid. Boil, cool, filter on Gooch crucible, and wash with water. Ignite, and weigh as zinc pyrophosphate. Calculate to zinc oxide.

197. Sulphates. Dissolve 0.5 gram in water 25 c.c., ammonia 10 c.c., hydrochloric and in slight excess.

Dilute to 200 c.c. and add a piece of aluminum foil which should about cover the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing

[1] The author is indebted to L. S. Hughes of the P[redacted]ublimed Lead Company for this method.

the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, boil, and precipitate as barium sulphate in the usual manner.

198. Sulphur dioxide. Treat 2 grams with 5 per cent sulphuric acid and titrate with $\frac{N}{100}$ iodine. A quick method of calculating the lead sulphate and oxide from the above data is the following: Multiply the weight of barium sulphate from 1 gram by 1.3, which gives the weight of lead sulphate. Multiply the same weight of barium sulphate by 0.088 and deduct this result from the total lead found. Multiply the difference by 1.077, which will give the lead oxide.

199. Composition of sublimed white lead. The approximate composition of sublimed lead as stated by the manufacturers is as follows:

	Per cent.
Lead sulphate	75
Lead oxide	20
Zinc oxide	5
	100

The lead sulphate and lead oxide are apparently combined as a white oxysulphate. The zinc oxide is incidental to the manufacture.

ANALYSES OF SUBLIMED WHITE LEAD BY THE AUTHOR.

	I. Per cent.	II. Per cent.
Lead sulphate	75.02	80.29
Lead oxide	18.48	14.46
Zinc oxide	6.22	5.18
Silica and alumina	0.28	0.07
	100.00	100.00

200. Sublimed blue lead. This pigment, which has a grayish blue color, is obtained in much the same way as sublimed white lead. Its variable and complex

composition, however, limits its use. The following is an analysis published by Mannhardt:[1]

	Per cent.
Lead sulphate	41.72
Lead sulphite	7.55
Lead sulphide	10.76
Lead oxide	29.03
Zinc oxide	2.84
Calcium oxide	2.88
Magnesium oxide	0.80
Ferric oxide	0.40
Carbon dioxide	0.86
Carbon	2.50
Bitumen	0.34
Moisture	0.50
	100.18

201. The identification and estimation of sublimed white lead in mixtures.[2] Neutral ammonium chloride solution will dissolve the lead compounds of sublimed white lead; also the hydrate of corroded white lead, zinc oxide, and some calcium sulphate. It leaves undissolved calcium carbonate, zinc sulphide, normal lead carbonate, and the content of lead carbonate in corroded lead.

To determine the sublimed white lead in a pigment containing the above ingredients, boil the sample with a considerable excess of strong neutral ammonium chloride solution, filter hot on the pump, and wash with hot dilute neutral ammonium chloride.

202. The lead, zinc, lime, and sulphuric anhydride are determined in the filtrate. The required sulphur trioxide is combined with the lime and the rest with the lead. Any excess of lead is contingent in its application upon the amount of lead found undissolved by the ammonium chloride.

If there is an appreciable amount of this residual carbonate, the required hydrate is calculated, and a

[1] Drugs, Oils and Paints, August, 1909.

[2] The author is indebted to L. S. Hughes for this method.

deduction made from the excess lead found in the filtrate. Any lead in the original filtrate not satisfied is now calculated to lead oxide and regarded as the lead oxide of sublimed white lead, and the lead sulphate and zinc oxide thereof calculated and deducted from the total of these compounds.

It will be noted that the conditions above considered are much more complex than need be anticipated in the analysis of actual paints.

Extraction of lead sulphate by the above treatment prevents the necessity of considering the sulphuric anhydride of possible barium sulphate, and leaves the original residue in such shape that if it contains both the carbonate and sulphate of barium they can be conveniently separated.

Analysis of Zinc Pigments.

203. Moisture. Two grams of the pigment are weighed out on a watch glass, provided with a cover glass and clip, dried for two hours in a steam oven, the cover glass placed in position and held by the clip, the glasses cooled in the desiccator and weighed. Loss in weight represents the amount of moisture in the pigment.

204. Silica. Weigh 1 gram of pigment into a 250-c.c. covered beaker, add 25 c.c. of concentrated hydrochloric acid, heat gently for five minutes, or until the pigment has dissolved (if lead sulphate is present in considerable quantity this may take quite a few minutes), add 50 c.c. hot water, and continue the heating for about five minutes longer. Filter boiling hot with the aid of suction, washing thoroughly with boiling water so as to remove all the lead and zinc salts from the filter paper. The filter paper and any

residue of silica is burned, ignited, and weighed in the usual manner. Any weighable residue is reported as silica.

205. This treatment may give results that are slightly low, owing to the slight solubility of silica in strong hydrochloric acid, but for commercial purposes this slight error may be neglected. In carefully prepared zinc pigments the amount of silica present will be unweighable; even with careless processing the amount will seldom exceed a very few hundredths of 1 per cent.

206. **Sulphur dioxide.** Weigh 3 grams of the pigment into a 250-c.c. beaker; add 100 c.c. of distilled water, that has been *recently boiled* and cooled. Add 5 c.c. of concentrated sulphuric acid, stir thoroughly, and allow to stand 15 minutes. Titrate with standard hundredth normal iodine solution, using starch paste as an indicator.

1 c.c. hundredth normal iodine = 0.00032 gram sulphur dioxide.

207. **Preparation of reagents — Iodine solution.** Dissolve 1.268 grams of pure iodine and 1.8 grams of potassium iodide in about 150 c.c. of water in a graduated liter flask. After solution, fill to the mark with water that has been freshly boiled.

208. **Sodium thiosulphate.** Dissolve 2.5 grams in recently boiled distilled water and make up to 1 liter. Preserve in a brown glass bottle or one that has received a liberal coat of asphaltum.

209. **Starch paste.** One gram of starch is boiled in 200 c.c. of distilled water.

210. **Standardizing the sodium thiosulphate solution.** Pipette 20 c.c. of standard potassium dichromate solution in a 250-c.c. beaker; add 10 c.c. of a 15-per cent

solution of potassium iodide. Add 10 c.c. of a 15-per cent solution of potassium iodide. Add to this 5 c.c. of strong hydrochloric acid. Allow the solution of thiosulphate to run in slowly from a burette until the yellow color has almost disappeared. Add a few drops of starch paste and continue the addition of thiosulphate with constant stirring until the blue color just disappears. The burette reading is then made and the value of the thiosulphate calculated.

211. Standard of acceptance. A good grade of zinc oxide should contain only a trace of sulphur dioxide. Many paint chemists reject oxides containing more than six hundredths of one per cent. The reason for this is that the sulphur dioxide affects the character of the linseed oil very strongly, causing the paint to thicken and ultimately "liver" in the package. This may be shown in an experimental way by dividing a sample of zinc oxide into two parts, exposing one part to an atmosphere of sulphur dioxide, then spreading equal amounts of both samples on a glass plate and mixing to a paste with the same number of drops of oil in exactly the same manner. It will be found that the sample containing the sulphur dioxide will be thicker and stiffer than the other, showing the effect of the sulphur dioxide on the oil.

212. Reaction with rosin products. In the presence of rosin products of any kind, such as are often used in the driers of mixed paints, sulphur dioxide acts as a contact agent of great strength, causing changes all out of proportion to the amount present, often resulting in hardening, "washing" of the paint film, "livering" in the package, etc. These results will be influenced to a considerable degree by the acidity, moisture, and temperature of the paint, and hence no hard and fast

deductions can be made as to what may be expected of any particular paint containing sulphur dioxide in excess of the prescribed amount.

213. **Zinc sulphate.** Ten grams of the pigment are weighed into a 250-c.c. Erlenmeyer flask and 100 c.c. of boiling water added. The contents of the flask are then shaken thoroughly for several minutes and filtered and the residue on the filter paper washed with several portions of boiling water. The soluble zinc in the filtrate is then titrated as described under the "Estimation of Zinc" by titration with ferrocyanide, and calculated to zinc sulphate.

214. It is not advisable to boil zinc oxide pigments with the water, as interaction may occur between the zinc oxide and any lead sulphate present, resulting in the formation of more zinc sulphate. Neither is it wise to estimate the soluble combined sulphuric acid in the hot aqueous filtrate and calculate to zinc sulphate, as there often seems to be an excess over what is required to form the normal sulphate of zinc and hence the results are apt to be too high.

215. **Effect.** Zinc sulphate is not considered by many paint chemists to be so objectionable in zinc pigments as sulphur dioxide, and is often permitted in amounts under 1 per cent. In amounts above 1 per cent it seems to act as an astringent on the oil when used in the preparation of mixed paints, tending to prevent the proper penetration of the wood, especially if the paint has been ground for some length of time. A prominent paint chemist discusses its effect as follows: "The action of zinc sulphate is twofold: first, as an astringent upon the oil and tending to cause a distinct demarcation between two coats; and second, that of a contact agent, facilitating reaction between the different pigments.

The visible results of its presence are peeling and 'washing.' Apparently, rather more than the normal amount of moisture must be present to cause its activity, and if the paint coat has set under dry or normal conditions, the zinc sulphate produces no apparent effect." In the exposure tests conducted by the author, the worst cases of "washing" have occurred with zinc pigments in which the sulphur dioxide was less than one-hundredth of 1 per cent and the zinc sulphate between 1 and 1½ per cent.

216. Lead. The lead present in zinc pigments is usually in the form of sulphate and may be estimated by either of the following methods.

217. Method I. The filtrate from the silica, which need not exceed 100 c.c. in volume if the washing has been judiciously conducted by suction or the hydrochloric acid solution is absent, is evaporated very nearly to dryness in an uncovered beaker on the hot plate, avoiding actual boiling, 10 c.c. of warm water added, and evaporated again nearly to dryness in order to expel the hydrochloric acid. Cool, add 30 c.c. dilute sulphuric acid, heat to boiling for five minutes in a covered beaker, cool, add 50 c.c. of alcohol, and allow to stand one-half hour or until all of the lead sulphate is precipitated from solution. Filter through a weighed Gooch crucible, washing thoroughly with 50 per cent alcohol, until the precipitate is entirely freed from zinc sulphate. Dry on hot plate, heat gently over a Bunsen burner, cool in desiccator, and weigh as lead sulphate. If heated over the flame before drying, a portion of the lead is liable to be reduced to lead oxide by the alcohol, and the weight will be low.

218. Method II. The lead may be separated from the zinc in a solution barely acid with hydrochloric acid, by

hydrogen sulphide, the precipitated lead sulphide dissolved in nitric acid and titrated with standard molybdate or bichromate solution, as described in Chapter XVI, Analysis of White Paints.

219. **Method III.** The amount of lead sulphate may be rapidly estimated by dissolving a weighed amount of the pigment in dilute acetic acid, filtering on to a weighed Gooch crucible, washing with warm water, heating gently, and weighing the lead sulphate direct. Lead sulphate being slightly soluble in acetic acid the results will be somewhat low and can only be considered as roughly approximate.

220. **Total zinc.** The zinc can be rapidly and accurately estimated volumetrically by the following methods.

221. **Potassium ferrocyanide method.** Preparation of reagents.

222. **Standard zinc solution.** Dissolve 10 grams of chemically pure zinc in hydrochloric acid in a graduated liter flask, add 50 grams of ammonium chloride, and make up to 1 liter.

1 c.c. = 0.01 gram zinc or 0.01245 gram zinc oxide.

223. **Standard potassium ferrocyanide solution.** Dissolve 46 to 48 grams of crystallized potassium ferrocyanide in water, make up to 1000 c.c.

224. **Uranium nitrate solution.** Dissolve 15 grams of uranium nitrate in 100 c.c. of water.

225. **Standardizing the ferrocyanide solution.** To determine the value of the potassium ferrocyanide solution, pipette 25 c.c. of the zinc solution into a 400-c.c. beaker. Dilute somewhat and make faintly alkaline with ammonia, bring to a faintly acid condition with hydrochloric acid, and then add 3 c.c. excess of the concentrated acid, dilute to a total volume of about

250 c.c., heat to 80° C., and titrate as follows: Pour off about 10 c.c. of the zinc solution into a small beaker and set aside, run the ferrocyanide into the remainder from a burette, a few cubic centimeters at a time, until the solution takes on a slight ash-gray color, or until a drop of the solution placed in contact with a drop of the uranium nitrate solution on a porcelain plate turns to a distinct brownish color.

226. Often the end point has been passed by quite a little. The 10 c.c. of zinc solution that has been reserved is now added and the titration continued, drop by drop, testing a drop of the solution carefully on the porcelain plate after each addition of ferrocyanide solution. Some little time is required for the test drop to change color, so that the end point may have been passed slightly; this may be corrected for by making a memorandum of the burette readings, having the test drops arranged in regular order, and taking as the proper reading the one first showing a distinct brownish tinge. Having noted the number of cubic centimeters ferrocyanide required for the titration of the standard zinc solution, the value of 1 c.c. may be readily calculated.

227. **Titration of sample.** One-half gram of the sample if high in zinc, or 1 gram if the zinc content is fairly low, is dissolved in a covered beaker in 10 c.c. of hydrochloric acid and 10 c.c. of water, the solution diluted somewhat, neutralized with ammonia, and treated exactly as described above for the standard zinc solution, care being taken to titrate to exactly the same depth of color on the porcelain test plate. If the method is carefully carried out, the procedure being uniformly the same in each determination, the results will be found satisfactorily accurate.

228. **Combined sulphuric acid.** Dissolve 0.5 gram to 1 gram of the pigment, according to the amount of sulphates present, in

Water, 25 c.c.
Ammonia, 10 c.c.
Hydrochloric acid, a slight excess.

229. Dilute to 200 c.c. and add a disk of aluminum foil, which should about cover the bottom of the beaker. Boil gently until the lead is precipitated, holding the disk if necessary to the bottom of the beaker with a glass rod. The completion of precipitation is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake and washing thoroughly to free from solution.

230. Add to the filtrate a few drops of bromine water, boil, and precipitate with barium chloride in the usual manner for sulphates. In order to avoid a possible reduction of a portion of the barium sulphate in the pores of the filter paper during its incineration, the precipitate may be filtered directly on to a Gooch crucible, which after being weighed has a disk of ashless filter paper placed on top of the customary asbestos felt. This will effectually prevent any of the precipitate from burrowing through the filter. The ignition of the precipitate in the presence of the small disk of filter paper will cause no appreciable reduction to sulphide.

231. **Calculations.** The amount of zinc present as sulphate of zinc is deducted from the total zinc and the remainder calculated to zinc oxide. The sulphuric acid combined with the zinc is deducted from the total combined sulphuric acid and the remainder calculated to lead sulphate. Any excess of lead over that required

to combine with the sulphuric acid is calculated to lead oxide. Unless sublimed lead is present there will be little or no lead oxide.

Undoubtedly new sulphate of lead pigments will be placed on the market within the next few years which will be entirely different from those discussed, and in such instances careful determinations of the service values should be made apart from the chemical examination.

CHAPTER XIII.

ANALYSIS OF SUBLIMED WHITE LEAD AND THE ZINC PIGMENTS (continued).

232. Zinc white. It was formerly the custom to offer reduced zinc oxides in oil, i.e., combination zincs under the name of *zinc white*, the different grades being distinguished by the use of such terms as "Green Seal, Red Seal," etc. Until the passage of suitable paint laws the purchaser had no means of knowing what he was obtaining, any more than he did in the case of combination leads which had hitherto been sold under the simple designation *white lead*. It is now customary for paint manufacturers to offer reduced zinc oxides under an explanatory designation like the following:

Zinc White.

In combination with reinforcing pigments. Ground in pure linseed oil. 12½ lbs. net weight.

Analysis.	Per cent.
. . . . .	. . .
. . . . .	. . .
. . . . .	. . .
	100.00

233. The analysis of reduced zinc oxides offers no difficulties except that when ground in varnish the determination of the constitution of the varnish will require careful consideration. Usually the varnish will be found to be dammar cut with turpentine or naphtha or both, and may be used in conjunction with varnish oil (a specially prepared linseed oil).

234. The following analyses are characteristic of the zinc whites on the market:

	I. Per cent.	II. Per cent.	III. Per cent.
Zinc oxide	53.93	69.61	61.83
Barium sulphate	35.96	18.99	8.03
Linseed oil	10.11	11.40	2.00
Turpentine	.....	.....	14.35
Dammar gum	.....	.....	13.79
	100.00	100.00	100.00

235. **Estimation of arsenic and antimony in zinc leads.** Weigh 2 grams of the sample into a 200-c.c. digestion flask. Add 7 grams of potassium bisulphate, 0.5 gram of tartaric acid, and 10 c.c. of concentrated sulphuric acid. Digest carefully at first, but finally with the full power of a Bunsen burner until a clear mass remains, containing but little free sulphuric acid. Cool, spreading the melt around on the sides of the flask. Add 50 c.c. of water, 10 c.c. of strong hydrochloric acid, and digest for about twenty minutes without boiling.

236. Cool thoroughly under the tap and filter off the separated lead sulphate. Dilute the filtrate to about 300 c.c. with hot water, maintain the liquid warm, and pass in hydrogen sulphide for about fifteen minutes or until precipitation is complete. Filter, washing with hydrogen sulphide water. Digest filter and contents in a rather small amount of yellow ammonium sulphide. Filter on suction cone, washing with as small a quantity of water as possible.

237. Digest the filtrate with 3 grams of potassium bisulphate and 10 c.c. of strong sulphuric acid over a free flame until all of the free sulphur and the larger portion of free acid are expelled. Cool, spreading the melt around on the sides of the flask as before. Add 25 c.c. of water and 10. c.c. of strong hydrochloric acid, and warm to effect complete solution. Cool under the

tap, add 40 c.c. of strong hydrochloric acid, and pass in hydrogen sulphide until complete precipitation of the arsenic takes place, — 15 to 30 minutes. The antimony remains in solution.

238. Filter off the precipitated arsenious sulphide on to a weighed Gooch crucible, washing with a mixture of two volumes of hydrochloric acid and one of water. The filtrate is reserved at this point for the estimation of antimony. The precipitate is next washed with alcohol, the crucible and contents placed in a small beaker, the crucible nearly filled with carbon bisulphide, and the contents allowed to digest at ordinary temperature for about twenty minutes in order to dissolve the free sulphur. The carbon bisulphide is removed by suction, the crucible dried in the steam oven, cooled, and the precipitate weighed as arsenious sulphide and calculated to arsenious oxide.

Weight arsenious sulphide $\times$ 0.8043 = weight arsenious oxide.

239. Instead of weighing as the sulphide, the arsenic may be estimated volumetrically as follows: Wash out the hydrochloric acid from the sulphide precipitate with hydrogen sulphide water. Digest filter and contents in a little warm ammonium sulphide, filter on a suction cone, washing with a little dilute ammonium sulphide solution. Place the filtrate in digestion flask, add 2 to 3 grams of potassium bisulphate and 5 c.c. of strong sulphuric acid. Evaporate, boiling to a small bulk, and then manipulate the flask over a free flame until the sulphur is entirely expelled and most of the free acid also. Take up, after cooling, by warming with 50 c.c. of water, and then boil sufficiently to expel any possible sulphur dioxide. Now drop in a bit of litmus paper as an indicator, and then add ammonia

until the solution is slightly alkaline. Again slightly acidify with hydrochloric acid and cool to room temperature. Finally, add 3 to 4 grams of sodium acid carbonate and a little starch liquor and titrate with standard iodine solution. Pay no attention to a slight discoloration toward the end, but proceed slowly until a single drop of the iodine produces a strong permanent blue color.

240. **Preparation of iodine solution.** The iodine solution may be prepared by dissolving about 11 grams of iodine in a little water with the addition of about 20 grams of potassium iodide and diluting to 1 liter. Standardize with arsenious oxide. Dissolve about 0.150 gram in 5 c.c. of strong hydrochloric acid by warming very gently, dilute and neutralize as described above, and finally titrate with the iodine solution. 1 c.c. of the latter will equal about 0.003 gram of arsenic.

241. **Antimony.** Very nearly neutralize the filtrate reserved for the antimony estimation with hydrochloric acid, dilute with double its volume of hot water, and pass in hydrogen sulphide until all of the antimony is precipitated. Filter, washing with hydrogen sulphide water. Digest filter and contents in a little ammonium sulphide, filter on suction cone, and wash with dilute ammonium sulphide. Place the filtrate in the digestion flask and add about 3 to 4 grams of (pure) potassium bisulphate and 10 c.c. of strong sulphuric acid. Boil as previously described to expel first the water, then all the free sulphur, and finally most of the free acid.

242. Cool, add 50 c.c. of water and 10 c.c. of strong hydrochloric acid. Heat to effect solution, and then boil for a few minutes to expel any possible sulphur dioxide. Finally add 10 c.c. more of strong hydrochloric

acid, cool under the tap, dilute to about 200 c.c. with cold water, and titrate with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations will answer. The oxalic acid value of the permanganate multiplied by 0.9532 will give the antimony value.

243. **Methods of determining small amounts of arsenic and antimony in use at Canon City, Colorado.** *Method I.* Take two or three grams of pigment and dissolve in 10 c.c. nitric acid and 10 c.c. sulphuric acid. Heat to expel the nitric acid and evaporate to sulphuric fumes. The advantage of the nitric acid is to oxidize the arsenic present and thereby avoid any loss of arsenious acid by volatilization. Allow to cool and dilute with cold water, then add about 50 per cent of the volume of alcohol to insure complete precipitation of all lead as lead sulphate. Filter and wash, boil filtrate to expel alcohol, and add about 10 to 15 c.c. of hydrochloric acid. Precipitate the warm solution with hydrogen sulphide. Filter and wash with dilute hydrogen sulphide water. All arsenic, antimony, and copper are on the filter as sulphides. Test filtrate with hydrogen sulphide as check on precipitation.

244. Dissolve the sulphides in caustic potash solution, then bring to a boil and pass hydrogen sulphide into warm solution as before. Filter and test filtrate. Wash with dilute ammonium sulphide solution. All arsenic and antimony are in filtrate and any copper present is on the filter. If any copper is present, dissolve and titrate by the iodide method.

245. Make filtrate acid with hydrochloric acid and add about 10 c.c. excess and pass in hydrogen sulphide gas as before. Filter off the sulphides of arsenic and antimony and wash with hydrogen sulphide water.

Dissolve these sulphides in about 10 c.c. aqua regia, then dilute with water and make alkaline with ammonia, adding about 25 c.c. excess. Then add from 1 to 2 grams tartaric acid and 10 to 15 c.c. magnesia mixture. Allow to stand over night. All the arsenic is precipitated as ammonium magnesium arsenate. Antimony remains in solution, being held there by the tartaric acid present. Filter off the ammonium magnesium arsenate, washing with cold water containing a little ammonia, then dry, ignite, and weigh as magnesium pyroarsenate.

246. Acidify the filtrate with hydrochloric acid and precipitate the antimony with hydrogen sulphide as before; filter and wash with hydrogen sulphide water. Separate the antimony sulphide from the filter paper and dissolve the adhering particles with ammonium sulphide, transferring to a beaker. Wash with ammonia and evaporate to dryness on water bath. Carefully add a few drops of nitric acid and 1 to 2 c.c. of fuming nitric acid to oxidize the antimony. Evaporate to small bulk for crucible, and heat to dryness in water bath, ignite at low red heat to constant weight.

247. *Method II.* Treat 10 grams of pigment in a No. 3–A casserole with about 10 grams potassium bisulphate, 10 c.c. nitric acid, 15 c.c. sulphuric acid, and about 0.5 gram tartaric acid. Run to strong fumes; continue heating until all the carbon is destroyed and the solution is clear. Cool, dilute, and boil until soluble sulphates are in solution. Cool, filter, and wash thoroughly. Add tartaric acid and pass hydrogen sulphide gas. Filter off arsenic and antimony sulphides. Dissolve precipitate in potassium hydroxide solution and filter. Pour filtrate into solution of hydrochloric acid (2 to 1). Pass hydrogen sulphide gas and filter

off As_2S_3 on a weighed Gooch crucible. Wash with alcohol and carbon bisulphide to remove sulphur.

248. Neutralize filtrate until Sb_2S_3 begins to precipitate. Dilute with equal volume of water, pass hydrogen sulphide gas, and filter off precipitate, Sb_2S_3, on a weighed Gooch crucible. Wash with alcohol and carbon bisulphide to remove sulphur. Dry and weigh.

249. ANALYSES OF LEADED ZINCS BY THE AUTHOR.

	I.	II.	III.
Moisture	0.03	0.02	0.04
Sulphur dioxide	0.30	0.29	0.50
Zinc sulphate	0.86	1.49	1.26
Lead sulphate	26.46	19.76	23.06
Zinc oxide	72.11	78.11	74.72
Undetermined	0.24	0.33	0.42
	100.00	100.00	100.00

	I.	II.	III.	IV.
Moisture	0.29	0.58	0.20	0.26
Sulphur dioxide	0.01	0.01	0.01	0.01
Arsenious oxide	0.68	0.47	0.32	1.60
Antimony oxide	0.20	0.33	0.20	0.88
Silica	0.14	.....	0.05	0.04
Zinc sulphate	0.78	0.55	1.61	0.84
Lead sulphate	46.00	48.80	46.66	49.82
Zinc oxide	51.70	49.15	50.90	46.48
Undetermined	0.20	0.11	0.05	0.07
	100.00	100.00	100.00	100.00

250. **Moisture.** *Analysis of lithopone, ponolith, etc.* Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

251. **Barium sulphate.** To 1 gram add 10 c.c. of hydrochloric acid and 10 c.c. of water, heat gently until excess of acid has been expelled, dilute with 100 c.c. of water, and boil gently for 10 minutes. Filter, ignite and weigh residue as barium sulphate.

252. **Total zinc.** Neutralize the filtrate from the barium sulphate with ammonia, make distinctly acid with hydrochloric acid, heat to about 80° C., and titrate

with standard potassium ferrocyanide as described in Chapter XVI.

253. **Zinc sulphide.** Fuse 1 gram in a larger crucible with a mixture of potassium nitrate and potassium chlorate for about half an hour. Dissolve the fused mass in dilute hydrochloric acid and boil the solution with a strong nitric acid for half an hour. Filter off the insoluble residue, precipitate the combined sulphuric acid in the filtrate with barium chloride in the usual manner, filter, ignite, and weigh.

Wt. barium sulphate $\times$ 0.1373 = wt. sulphur.

Calculate sulphur to zinc sulphide.

254. **Zinc oxide.** Calculate excess of zinc over what is required to form the zinc sulphide to zinc oxide.

255. **Calcium.** Occasionally zinc sulphide whites are found on the market in which the barium sulphate has been wholly or partially replaced with calcium sulphate. In which case the calcium is estimated in the usual manner, after the removal of the zinc as sulphide, and the sulphuric acid combined with the calcium determined as usual. The sulphuric acid due to the calcium must be deducted from the total sulphuric acid obtained by oxidation before calculating to zinc sulphide.

256. ANALYSES OF ZINC SULPHIDE WHITES BY AUTHOR.

	I. Lithopone.	II. Ponolith.
Moisture	0.20	0.18
Barium sulphate	69.62	69.19
Zinc sulphide	28.05	28.07
Zinc oxide	1.55	2.27
Undetermined	0.58	0.29
	100.00	100.00

CHAPTER XIV.

DETERMINATION OF FINENESS, COVERING POWER AND TINTING STRENGTH OF PIGMENTS.

257. Determination of the comparative fineness of pigments. The comparative fineness, or perhaps better, the rate of settling of pigments, may be determined by means of the following apparatus:

A is an ordinary graduated cylinder holding 100 c.c.

B is a black metal shield attached to the block *D*, which half surrounds the cylinder, and is provided with a round opening $\frac{3}{16}$ of an inch in diameter, exactly opposite the 25 c.c. graduation.

C is an electric light.

258. The cylinder is filled to the 100 c.c. mark with 87 degrees gasoline; 2 grams of the pigment to be tested are introduced, the cylinder stoppered, shaken 25 times with a uniform motion, and the stop watch started with the last shake. The cylinder is placed in position and the time noted until the outlines of the aperature can be plainly observed. This gives an excellent method of determining the comparative fineness of pigments of the same type.

259. Comparison of paints for covering power. The following method described by G. W. Thompson, though open to criticism, furnishes in many cases much valuable data:

"Use white pine boards, 30 inches long by 10 inches wide, and approximately 1 inch thick. Each end of the board is provided with a cleat having a tongue fitting into a groove on the end of the board and

securely nailed on. The entire board, including the cleats, to be finished to the size given above. Three of these boards may be primed with, say, the following paint mixture:

White lead paste	100 lbs.
Linseed oil, — ⅓ boiled	75 lbs.

No attempt is made to secure a definite amount of priming paint to the unit of surface; this, for the

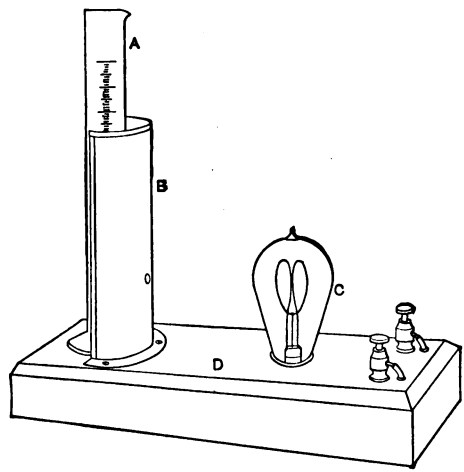

FIG. 6.

reason that the boards may vary considerably in their absorptive power. When this priming coat is dry, each board receives a diagonal stripe of lampblack in japan about 1 inch wide on one or both sides of the board, as may be desired. When this black stripe is dry it is given a second coat of paint mixed to a consistency proper for painting, the formula being recorded.

260. "The weight per gallon of the paint so mixed is then obtained by finding its specific gravity and multiplying by 8.33, which gives the weight per gallon.

Inasmuch as the board used has a total surface of 680 square inches, all that is required to be done is to find what the ratio is between 680 square inches and the spreading rate at which it is desired to apply the paint in order to find the fraction of the gallon to be applied to each board. If the rate adopted is 1200 square feet to the gallon, then we get the formula:

$$680 \text{ sq. inches} : 1200 \text{ sq. feet} : : 1 \; . \; . \; x,$$

the reciprocal of 'x' being the fraction of a gallon of paint to be applied to each board, one coat. Having the weight of the paint per gallon we easily get the amount of paint by weight to apply to each board, one coat on all sides. When this second coat of paint is thoroughly dry, a similar coat is applied; and, when dry, the boards can be compared for the covering power of the paints on them. We mention the painting of three boards with each paint to be compared. The purpose of this is that variations in results are obtained between boards which are apparently painted in an identical manner. These variations are not great, but it is thought best to eliminate them, to a certain extent, by painting three boards and selecting the one giving medium results for comparison with boards painted with other paints."

261. Determination of the tinting strength of colors. The determination of the tinting strength of color pigments is a very necessary operation in the valuation and use of color pigments. The colors should always be compared with a carefully selected standard.

262. Chrome yellows, ochres and greens. Weigh out 0.05 gram of color, place on a large glass plate, add 12 drops of bleached linseed oil, and rub up with a flat-bottomed glass pestle or muller, then add 1 gram of

zinc oxide, kept solely for this purpose, and grind with a circular motion fifty times, gather up with a sharp-edged spatula and grind out twice more in like manner, giving the pestle a uniform pressure.

Weigh out 0.05 gram of the color kept as the standard, and treat in exactly the same manner as described above. Transfer the standard to a microscope slide and spread out evenly, drawing the spatula in one direction only, and that toward the end of the slide. In like manner transfer the prepared sample to the slide, spread out evenly as before, drawing the spatula in the same direction as directed above, and bringing the edge of sample carefully to the edge of the standard. Compare the tints as shown on both sides of the glass.

263. Reds, red oxides, etc. Use 0.02 gram of sample to one gram of zinc oxide.

264. Blues and blacks. Use 0.01 gram of sample to 2 grams of zinc oxide with 24 drops of oil.

265. Paste goods. For testing the strength of paste goods a can containing pure zinc oxide ground in bleached linseed oil should be kept on hand.

266. Chrome yellows, ochres and greens. Use 0.5 gram of sample to 10 grams of zinc paste. Weigh accurately on balanced glasses and grind as described above.

267. Reds, red oxides, etc. Use 0.2 gram of sample to 10 grams of zinc oxide paste.

268. Blues and blacks. Use 0.05 gram sample to 10 grams of zinc oxide paste.

209. GRAVITY AND VOLUME OF PIGMENTS.[1]

Name of Pigment.	Sp. Gr.	Volume Loose Pigment, wt. per gal. in lbs.
White lead, Dutch Process	6.750	15.17
Sublimed lead	6.396	11.18
Zinc lead	5.635	6.64
Lead sulphate	6.082	9.77
Zinc oxide, Green Seal	5.470	3.57
Zinc oxide, selected	5.554	6.36
Lithopone	4.236	8.80
Barytes, domestic	4.482	16.96
Barytes, blanc fixé	4.329	12.95
Eng. C. S. Paris white	2.705	6.85
Precipitated chalk	2.580	2.82
Terra Alba, French	2.358	6.74
Silica, floated	2.596	6.47
Silica, ground	2.550	4.40
English china clay	2.596	3.83
Talc	2.749	6.72
Chrome yellow, light	6.413	6.12
Chrome yellow, medium	5.842	6.57
Chrome yellow, deep	5.910	12.06
Litharge, yellow	8.663	32.21
Litharge, red	8.781	24.07
Rochelle ochre	2.802	5.61
Red lead, English	8.681	26.22
Tuscan red, dark	3.660	12.76
Chrome green, light	5.754	11.51
Chrome green, medium	5.239	13.05
Prussian blue	1.956	2.83
Chinese blue	1.903	3.85
German ivory black	2.619	4.55
Frankfort black	2.935	6.17
Bone black	2.319	5.19
Graphite	2.293	8.69

[1] Drugs, Oils and Paints, Vol. XXI, page 299.

CHAPTER XV.

THE PRACTICAL TESTING OUT OF PAINTS.

270. Paints should be tested out by the chemist. The chemical analysis of a can of paint will tell much regarding the value of that paint, but a thorough practical testing out on a suitable surface will tell more, and the two in conjunction should render the chemist's report complete and above question. Often, however, the testing out is done by a so-called "practical man" who has little or no knowledge of chemistry, and his report for that very reason is apt to be misleading to the chemist. In order to secure the most desirable results, the chemist should do his own testing out, and this involves a practical painting knowlege that can be gained only by experience and under the guidance of an able master painter.

271. Equipment. The chemist, if he is to do his own testing out, should provide himself with an ample equipment so that he may carry on his work unhampered. He should have mixing cans large enough to hold sufficient paint for the coat to be applied and to allow stirring without danger of slopping over the side. A number of flat paddles of suitable sizes, a set of measures and a strainer, are also essential articles. All paint from the priming to the finishing coat should be strained, as it assists in securing a more uniform mixture than can be obtained by stirring. This is especially necessary where tints are to be tried out.

272. The chemist should be provided with a good set of brushes. It is a serious mistake to work with too

few brushes. For ordinary testing, the author believes that oval brushes should be used, and never a large flat brush which simply mops the paint on and does not assist it in penetrating into the fibres of the wood. An oval brush, being necessarily stiffer, rubs the oil and pigment into the wood, thoroughly satisfying it. For trimming and finishing the edges, a good chiseled varnish brush can be used with advantage. Having provided himself with a good set of brushes, the paint chemist should take good care of them. New brushes should never be placed in water. At the close of the day's work they may be laid out full of paint on a board, but should not be left this way for more than twenty-four hours. When through with the brushes for a time, they should be laid in a regular paint trough, containing raw oil, or they may be suspended in a can of raw oil containing a little turpentine, to prevent the oil from becoming fatty. They should not be allowed to stand on end, as it turns the painting edge of the brush. Neither should brushes be allowed to remain for long intervals in cans of paint. Brushes should never be allowed to get "lousy" through the paint drying on the bristles. In use, the brush should be handled in such a manner as to wear the bristles to a chisel edge-like point, and should never be jabbed into corners, but carefully worked in.

273. The requisites for a paint. The requisites for a high-grade paint are:

a. Covering power.
b. Spreading capacity.
c. Durability.
d. Wearing evenly.
e. Failing by gradual wear, and
f. Leaving a good surface for repainting.

In order to test out a paint to determine to what degree it will fulfill the above requirements, the chemist must have a clear understanding of the practical application of paint and the suitability of different surfaces to receive paint of varying consistencies.

274. Relation of the surface to the paint. The surface on which the paint is to be tested out is of prime importance, as it vitally affects the oil and turpentine reduction which should be given the paint. If the surface is a dense close-grained wood, a much more liberal turpentine reduction must be used than when the surface is more porous, as in the case of soft pine. The lumber used should be well seasoned and entirely free from dampness; and for outside paints, the surface should be exposed to the direct rays of the sun for at least a couple of days before applying the paint, even if the surface is apparently free from moisture. If the test is to be applied on a new building, every precaution should be taken that the lumber has dried out thoroughly after the plastering has been done. It must be remembered that there are eighty to ninety gallons of water in every hundred square yards of plaster, and if the house is kept closed during the time the plaster is drying, the moisture must pass through the clapboard siding, over which the paint is to be spread, in order to escape. This operation is much slower and takes a great deal longer time for completion, than most paint men believe. This is especially true if the house is sheathed with one or more thicknesses of paper between the boarding and siding. If the tests are to be placed on small test frames, such as are described below, or on specially constructed test fences, the conditions affecting the application of the paint can be more easily controlled.

275. Test structures. A convenient, practical, and efficient method of conducting exposure tests is shown in the illustration at the beginning of this book, which represents the first of a series of tests which are being conducted by the North Dakota Government Experiment Station.

This structure is 75 feet in length, 6 feet 6 inches high, begins 15 inches from the ground, and faces east and west. The posts are 5 feet apart and bedded in concrete. One side of the structure is plain boarded, the other side clapboarded, the top capped, and the ends boxed in a suitable manner. Four kinds of lumber were used in the construction, representing four of the most common varieties used for house building, and were securely nailed to studding set 1 foot and 8 inches apart. The structure was divided off into sections 16 inches wide and 5 feet in length, giving sufficient surface for the careful brushing out of the paint; each type of paint being applied over the four kinds of wood, and the work being three coats in each case. Twenty-one mixed paints and white leads were applied on this fence, representing prevailing types of combinations.

Figure 7 represents a second series of exposure tests begun during the summer of 1907. These fences are like the one described above, except that they are each 100 feet in length. There is a four-inch air space between the two surfaces of each fence, the numerous crevices between the boards permit of free circulation of air, and insure the prevention of continued dampness on the inside of the structure. Figure 8 illustrates the framework to which the boards and siding were nailed.

276. A more convenient method for making exposure tests, the painting of which may be done in the

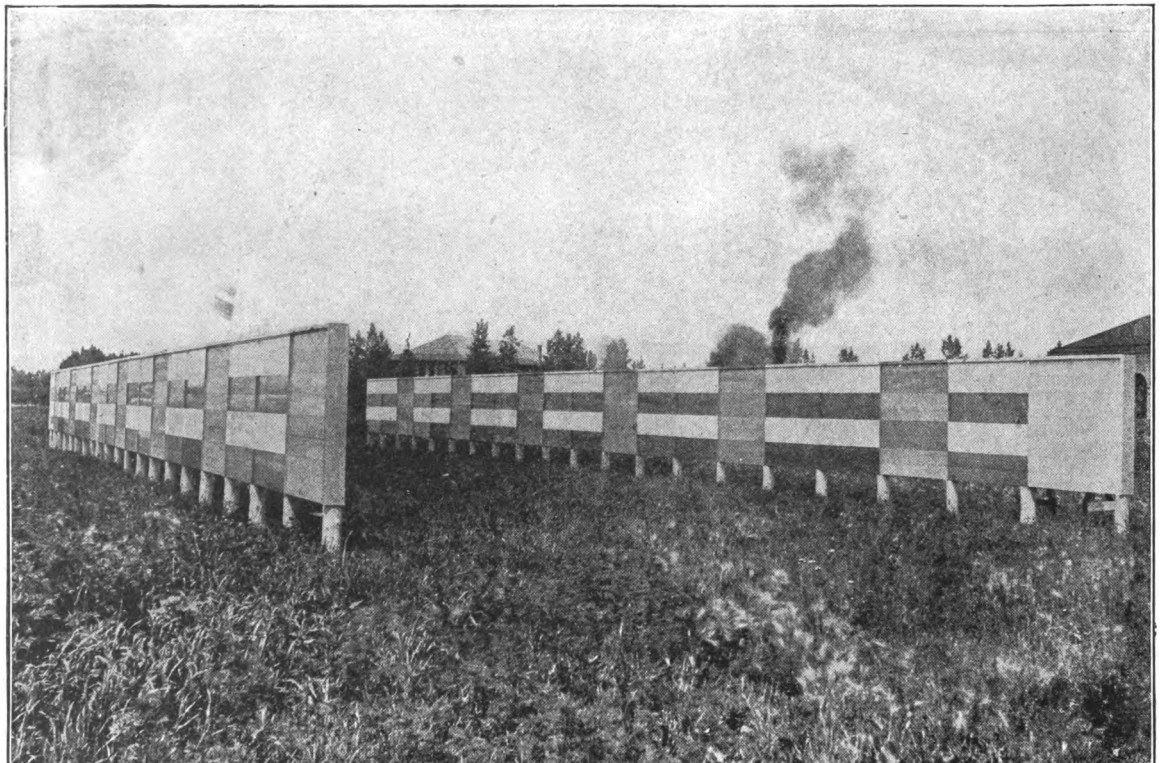

FIG. 7.—EXPOSURE FENCES, 1907.

FIG. 8. — FRAMEWORK OF TEST FENCES.

laboratory, is illustrated in Fig. 9. These test frames, so-called, have the additional merit of being easily transported from one place to another for inspection. These frames are 3 feet in length and 16 inches in width, the edge of the upper clapboard projecting half an inch above the cleats, and the lower clapboard set out a

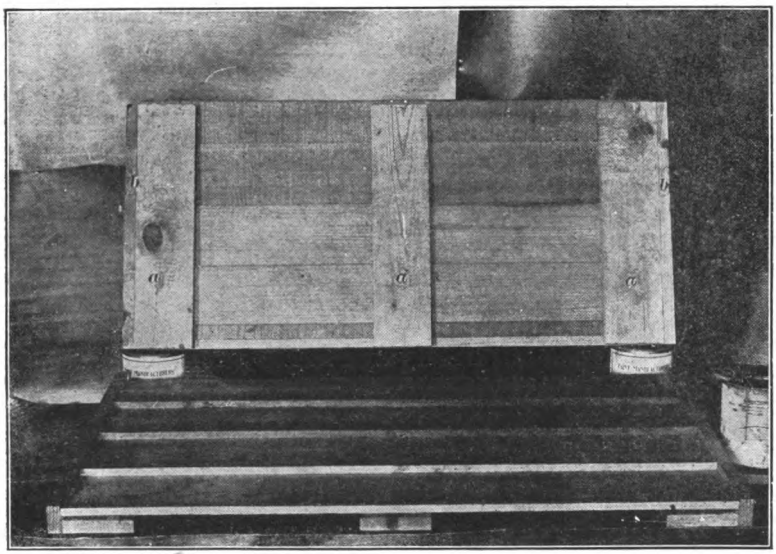

FIG. 9. — PORTABLE TEST FRAMES.

little, so that two or more frames may be put together, forming a unit surface exactly similar to the side of a house. These frames are made to be screwed to a framework like that illustrated in Fig. 8. The clapboards, four in number, are set four inches to the weather and are of two kinds of wood. The arrangement of the back cleats *a*, *a*, *a* and the end strips *b*, *b* through which the screws are inserted to hold the

frame to the skeleton fence, are clearly shown in the illustrations.

These end strips serve a much more important purpose, and one which makes the tests much more valuable than on a plain board surface, in that it tests out the brushing qualities of the paint very thoroughly. A poor paint will often brush out satisfactorily on an ordinary flat section of board, but will at once show its inferior quality when the painter attempts to work it into the corners and brush it away from the end strips, on the clapboard surface. In fact, it closely reproduces the actual conditions which the painter would encounter in applying the paint on an average house.

277. Application of the priming coat. In order to secure the best results with any given paint, three coats should be applied; of these three the most important is the priming coat. It compares with the foundation of a house, which, if not solidly and firmly constructed, renders the whole superstructure unstable. The priming coat, if not bedded thoroughly in the wood, will not serve to anchor and firmly bind the two additional coats to the surface. The essential consideration with the priming or first coat is to secure suitable penetration into the wood. In other words, the wood must be thoroughly satisfied. The necessity of this is explained with great force and clearness by J. B. Campbell, in his work entitled "Practical Painting."

278. The paint to be tested out, if of the ready mixed type, should be thoroughly "broken up," first pouring off the oil portion, stirring the residue until free from lumps, and then gradually working the oil portion back into the paste. This is best accomplished by removing the entire contents of the can into a larger mixing can, kept solely for this purpose. The consistency of the

paint after being "broken up" should be carefully noted, whether it is thin, medium, or heavy, as the amount of reduction which the paint will stand depends largely on its consistency.

279. Raw linseed oil should almost without exception be used instead of boiled oil for reducing the paint for the priming coat. Raw oil dries slowly and from the bottom up, which allows it to be thoroughly absorbed and to harden uniformly. Boiled oil does not penetrate the wood, owing to its rapid drying qualities, and hence the coating formed is a surface coating only, and does not become firmly anchored to the wood. Turpentine should be used liberally in the priming coat, as, by reducing the specific gravity and rendering the oil more mobile, it assists it in penetrating into the deeper pores of the wood, thus securing increased penetration and also more rapid drying. The harder and closer grained the wood, the larger the amount of turpentine required.

280. The following oil and turpentine reductions[1] will enable the chemist to judge the reduction required in most cases.

281. **Oil reductions.** "A full oil reduction consists of oil only, with the exception of $\frac{1}{32}$ gallon of turpentine to the gallon of paint, to assist in penetration; this is not enough turpentine to destroy the luster of the paint, and will accomplish the purpose of penetrating a hard or glossy surface where it would be unsatisfactory to apply paint without the addition of a small percentage of this thinner."

282. "A liberal oil reduction consists of seven eighth oil and one eighth turpentine to form the total amount of reducers; this amount of turpentine will cause more

[1] Campbell, Practical Painting, p. 63.

rapid and even penetration, but will not destroy the luster of heavy-bodied paint."

283. "A medium oil reduction consists of three fourths oil and one fourth turpentine to form the total amount of reducers; this amount of turpentine will destroy part of the luster and cause deep penetration on a hard surface."

284. **Turpentine reductions.** "A full turpentine reduction consists of nothing but turpentine, and is used for producing a flat paint."

285. "A liberal turpentine reduction consists of seven eighths turpentine and one eighth oil, to form the total amount of reducers."

286. "A medium turpentine reduction is half turpentine and half oil."

287. "Dark shades require more turpentine to produce the same results, as to penetration and flattening the paint, than light shades. Zinc and combination paints require more turpentine than strictly pure lead to produce the same results, as to destroying the luster of the paint. Where light shades require $\frac{1}{8}$ gallon of turpentine to produce the desired results as to flattening or destroying the luster and securing penetration, dark shades require $\frac{3}{16}$ of a gallon to produce like results."

288. It is also well to remember in making the reduction that turpentine reduces twice as fast as raw oil. The consistency to which the paint should be reduced for priming must necessarily be left to the judgment of the person applying it, and hence no definite directions can be given, but the following directions given by Campbell[1] have been found very helpful by the author.

289. "In priming soft wood, the paint should be applied with a full brush, and enough paint used at all

[1] Practical Painting, p. 69.

times to satisfy the surface. It should be well brushed, and especially on the harder grain, to assist or force the paint into this close grain, and remove by hard brushing any surplus paint that remains on the surface. On hard or close-grained wood a medium full brush should be used in applying the paint, as this class of wood does not possess the absorbing properties of softer woods, but requires more brushing in order to force a sufficient amount of oil and binder into the wood and at the same time not leave an excess of paint on the surface."

290. "If the priming coat is of the proper consistency, carrying sufficient pigment to fill and hide the grain, and well brushed into the wood, most of the absorption will have ceased with this coat and no excess of pigment be left on the surface. This thin coat will allow the second coat to penetrate through and satisfy any part of the wood which was not fully filled at the time of priming, and also allow the second coat to bind itself to the wood and priming coat."

291. **Application of the middle coat.** The priming coat should be given ample time to dry before applying the second coat, which, as Mr. Campbell states with much truth, should be "considered the medium between the foundation coat and the protecting or finishing coat." Careful judgment should be exercised in preparing the paint for this coating. "It must not be too elastic, and should dry firm without a high gloss. Too heavy an oil reduction will leave a high, glossy surface, over which the finishing coat will not adhere or properly dry." Sufficient turpentine should be used to secure the necessary penetration into the priming coat and to "flatten" out the paint so that it will show little or no gloss after 48 to 72 hours. Over such a surface the finishing

coat can be applied evenly, smoothly, and with great adherence. The directions for application as issued by most paint manufacturers are apt to fall short in the amount of turpentine necessary for the proper application of the second coat.

292. Nail holes and cracks should be carefully puttied. Cheap putty should be avoided, as it is apt to turn yellow and ultimately crumble and fall out. It is often better for the paint chemist to make his own putty, using medium whiting, raw oil, and paste white lead to about 20 per cent of the whiting used. The mixture should be carefully kneaded and worked until of stiff consistency.

293. If the work is to be only two-coat, the paint should have a full oil reduction, so as to insure sufficient elasticity and opacity, and should be worked out well under the brush.

294. **Application of third coat.** The paint for this coat should be of good consistency, with a full raw-oil reduction, so that it may be brushed out smoothly and evenly, and be sufficiently elastic so as to withstand severe exposures. Too much importance cannot be placed on the thorough brushing of the paint, as the durability and protection it affords are dependent to a great extent upon the thoroughness with which this is done. Paint flowed on will soon crack and come off, while, if plenty of muscle is used, it will make the finishing coat adhere more firmly to the second coat.

295. **Application of paste leads and paste paints.** In testing out paste paints and leads some convenient method should be adopted for calculating the amount of oil used in gallons per hundred pounds of paste. One of the simplest schemes is to weigh out the leads or pastes in $12\frac{1}{2}$ oz. quantities or multiples thereof. Then

each ounce of oil used is equivalent to one gallon per hundred pounds of paste.

One gallon is equivalent to 128 oz.

One hundred pounds are equivalent to 1600 oz.

$$1600 \div 128 = 12.5$$

In this way the necessary quantities of turpentine and drier can be rapidly calculated and measured out. For instance, if a specification to be tested out read,

100 lbs. white lead,
7 gal. raw linseed oil,
$\frac{1}{2}$ gal. turpentine,
$\frac{1}{8}$ gal. turpentine drier,

the above scheme would call for

$12\frac{1}{2}$ oz. white lead,
7 oz. raw linseed oil,
$\frac{1}{2}$ oz. turpentine,
$\frac{1}{8}$ oz. turpentine drier.

If larger amounts were required, the necessary multiple of $12\frac{1}{2}$ should be used and the other figures increased accordingly.

296. Driers. The proper use of driers is often a perplexing problem with the paint chemist. Campbell [1] says: "A wide experience with the products as used by the painter shows the greatest possible difference between them. Some of them are sufficiently powerful so that even 5 per cent added to raw oil is enough to cause it to dry as fast as with boiled oil, and not only that, but to dry throughout or from the bottom up, and not merely surface dry, as will boiled oil. Others again are so loaded with rosin and petroleum products and so deficient in true drying properties that 25 per cent or

[1] Practical Painting, p. 66.

more is required to accomplish this result, and then the resulting surface will be spongy or brittle, as the case may be, but in any event lacking in durability." In the face of these conditions the only recourse left the chemist is to test out his driers thoroughly, as described in a later chapter."

297. "The Japan or drier should be mixed with the paint while it is in semipaste form. The mixing is thus uniform and the results satisfactory. If an attempt is made to add it after the paint is ready for the brush, the Japan is liable to curdle; it will be difficult to mix uniformly and the resulting work is liable to be spotted, drying flat in some places and glossy in others." It should be borne in mind that paints containing zinc or dark colors will require more Japan than white lead alone, provided that it is essential to dry in a given time.

CHAPTER XVI.

ANALYSIS OF WHITE PAINTS.

298. Qualitative analysis. In the majority of cases a complete qualitative analysis of the pigments present is hardly worth the time it requires, as there is but little time lost in following the regular quantitative scheme. If, however, a qualitative analysis is desired, the following outline will be found sufficient in most instances, the removal of the vehicle previous to these tests being understood.

299. Carbonates. Effervescence with concentrated hydrochloric acid indicates carbonates, or hydrogen sulphide if zinc sulphide be present, the latter being distinguished by its odor and by the fumes blackening a piece of filter paper moistened with lead acetate.

300. Barytes, silica, clay, or other silicates. Boil above mixture five minutes, dilute with boiling water, filter. An insoluble residue may be barytes, silica, clay, or other silicates. Test for barytes with flame test, using a platinum wire. A characteristic green color indicates barium.

301. Sulphates. Test a small portion of the acid filtrate for combined sulphuric acid with a few drops of barium chloride.

302. Lead. Test another small portion of the acid filtrate with sulphuric acid. A white precipitate at once, or on standing indicates lead.

303. Zinc. Take another small portion of the acid filtrate and add a few drops of potassium ferrocyanide. A white precipitate with a bluish tinge indicates zinc.

304. **Calcium.** The remaining portion of the acid filtrate is made alkaline with ammonia and hydrogen sulphide passed in for five minutes. Filter and test filtrate for calcium with ammonium oxalate, setting aside in a warm place.

305. **Magnesium.** After completely precipitating the calcium add a few drops of hydrogen sodium phosphate. A precipitate on standing indicates the presence of magnesium compounds.

The identification of the forms in which the lead may occur can only be determined by the quantitative scheme if both sulphates and carbonates are present.

Quantitative Analysis of White Paints.

306. **Total lead.** Weigh 1 gram of the dry pigment into a 250 c.c. beaker. Add 30 c.c. of strong hydrochloric acid, boil 5 minutes, add 50 c.c. of hot water, heat 15 minutes longer, settle, filter while hot, and wash thoroughly with boiling water. The washing should be begun the instant the solution has filtered through, in order to avoid any crystallization of lead chloride in the pores of the filter paper. Once formed the crystals can only be dissolved with difficulty and with the use of an excess of wash water, which, as stated, must be at boiling temperature. This operation is best conducted by the aid of suction. Casein and other products of a similar nature are occasionally used in the manufacture of mixed paints in considerable quantities, and the analyst should always be on the lookout for the possible presence of these substances.

307. The solution is made just alkaline with ammonia, then just acid to litmus with hydrochloric acid. It is very necessary that the solution be only barely acid,

as a comparatively small quantity of free acid will keep considerable lead from precipitating. Having been made barely alkaline, which is indicated by the precipitation of the lead, the solution is brought to a faintly acid condition by using dilute hydrochloric acid (1 to 10). Dilute to about 350 c.c. Cool, pass in hydrogen sulphide gas, noting the color of the precipitate: if gray, some zinc is being thrown down; if reddish black, the solution is too acid. Add a few drops of dilute acid or ammonia as the case requires. Settle, filter, and wash with cold water.

308. Place filter and precipitate in 25 c.c. of nitric acid and 25 c.c. of water, heat gently until the lead has all dissolved, as shown by the residual sulphur having a yellow to whitish color. Do not boil hard enough thoroughly to disintegrate the filter paper. If difficulty is experienced in dissolving the lead contained in the sulphur particles, it is better to collect them into a ball with the aid of a stirring rod and remove to a small beaker and treat with a few cubic centimeters concentrated nitric acid, and heat until dissolved, then pour back into the larger beaker.

309. Pour solution and filter paper on to a suction funnel provided with a platinum cone. If any fine particles pass through, pour the filtrate back again. This procedure permits the washing of the filter mass with a very small amount of water, thus saving considerable time in the subsequent evaporation. Add 5 c.c. of dilute sulphuric acid to filtrate, and evaporate until sulphur trioxide fumes appear. Cool, add 25 c.c. of water, 25 c.c. of alcohol; allow to stand one-half hour with occasional stirring; filter, using Gooch crucible, wash with dilute alcohol, dry, heat gently over ordinary lamp, and weigh as lead sulphate.

310. **Calcium.** The filtrate containing the zinc, calcium, and possibly magnesium is made slightly alkaline with ammonia, a few drops of a mercuric chloride solution (1 to 10) added, and a stream of hydrogen sulphide gas passed into the solution for about ten minutes.

The addition of the mercuric chloride renders the precipitate granular and very easy to filter, and entirely obviates the difficulty of filtering a slimy zinc sulphide precipitate. In the analysis of tints where the zinc cannot be titrated until it has been freed from iron, the addition of the mercuric chloride will not cause any trouble, as treatment with hydrochloric acid results in the solution of the zinc only, the mercuric sulphide being insoluble in hydrochloric acid. Settle, decant, filter, and wash.

311. Evaporate the filtrate from above precipitate to about 150 c.c., make alkaline with ammonia, add ammonium oxalate (50 c.c. for 1 gram of lime), usually 20 c.c. is sufficient, and set in a warm place for two or three hours. Filter, wash, ignite, and weigh as calcium oxide, or titrate precipitate with permanganate by placing filter and the thoroughly washed precipitate in a 400 c.c. beaker, adding 200 c.c. of boiling water and 25 c.c. of dilute sulphuric acid, and titrate with standard tenth-normal potassium permanganate.

1 c.c. tenth-normal permanganate = 0.0028 gram CaO.
1 c.c. tenth-normal permanganate = 0.0050 gram $CaCO_3$.

Barium carbonate is still to be found in certain mixed paints, and it is advisable to test for the presence of soluble barium with a few drops of sulphuric acid before precipitating the calcium.

312. **Magnesium.** The filtrate from the calcium oxalate should be tested for magnesium by treating with

hydrogen sodium phosphate. Allow to stand one-half hour, add 25 c.c. of ammonia, allow to stand one hour, then filter on to a Gooch crucible, wash with dilute ammonia, ignite, and weigh.

Weight precipitate $\times$ 0.7575 = weight magnesium carbonate.

313. **Zinc oxide. Reagents. Standard zinc solution.** Dissolve 10 grams of chemically pure zinc in hydrochloric acid in a graduated liter flask, add 50 grams of ammonium chloride, and make up to 1 liter.

1 c.c. = 0.01 gram zinc or 0.01245 gram zinc oxide.

314. **Standard potassium ferrocyanide solution.** Dissolve 46 to 48 grams of crystallized potassium ferrocyanide in water, make to 1000 c.c.

315. **Uranium nitrate solution.** Dissolve 15 grams of uranium nitrate in 100 c.c. of water.

316. **Standardizing the ferrocyanide solution.** To determine the value of the potassium ferrocyanide solution, pipette 25 c.c. of the zinc solution into a 400 c.c. beaker. Dilute somewhat and make faintly alkaline with ammonia, bring to a faintly acid condition with hydrochloric acid, and then add 3 c.c. excess of the concentrated acid, dilute to a total volume of about 250 c.c., heat to 80° C., and titrate as follows: Pour off about 10 c.c. of the zinc solution into a small beaker and set aside, run the ferrocyanide into the remainder from a burette, a few cubic centimeters at a time, until the solution takes on a slight ash-gray color, or until a drop of the solution placed in contact with a drop of the uranium nitrate solution on a porcelain plate turns to a distinct brownish color. Often the end point has been passed by quite a little.

317. The 10 c.c. of zinc solution that has been reserved is now added and the titration continued, drop

by drop, testing a drop of the solution carefully on the porcelain plate after each addition of ferrocyanide solution. Some little time is required for the test drop to change color, so that the end point may have been passed slightly. This may be corrected for by making a memorandum of the burette readings, having the test drops arranged in regular order and taking as the proper reading the one first showing a distinct brownish tinge. Having noted the number of cubic centimeters of ferrocyanide required for the titration of the standard zinc solution, the value of 1 c.c. may be readily calculated.

318. **Titration of sample.** One-half gram of the sample, if high in zinc, or 1 gram, if the zinc content is fairly low, or the zinc sulphide precipitate obtained in section 310, is dissolved in a covered beaker in 10 c.c. of hydrochloric acid and 10 c.c. of water, the solution diluted and treated exactly as described above for the standard zinc solution, care being taken to titrate to exactly the same depth of color on the porcelain test plate. If the method is carefully carried out, the procedure being uniformly the same in each determination, the results will be found satisfactorily accurate.

319. **Lead sulphate.** Dissolve 0.5 gram in water, 25 c.c. hydrochloric acid in light excess. Dilute to 200 c.c. and add a piece of aluminum foil which about covers the bottom of the beaker. It is important that this be held at the bottom by a glass rod. Boil gently until the lead is precipitated. Completion of this is shown by the lead ceasing to coat or cling to the aluminum. Decant through a filter, pressing the lead sponge into a cake to free it from solution. Add to filtrate a little sulphur-free bromine water, ignite, and weigh as barium sulphate. Calculate to lead sulphate by multi-

plying by 1.3 as a factor, unless calcium sulphate is present, in which case it is advisable to make use of Thompson's separation.

320. In the absence of barium sulphate the combined sulphuric acid may be estimated by H. Mannhardt's method: Grind 1 gram of pigment with 1 gram of sodium carbonate very intimately in an agate mortar. Boil gently for ten minutes, the combined sulphuric acid, and in the case of colors containing chromates the chromic acid, will pass into solution and may be estimated in the filtrate in the usual manner. If necessary collect the insoluble portion on a filter, dry, detach, and triturate a second time.

321. **Basic carbonate of lead (white lead).** After deducting the amount of lead present in the pigment as sulphate of lead, calculate the rest of the lead as white lead by multiplying the remaining sulphate by 0.852, unless sublimed lead is suspected to be present, in which case the combined lead oxide must be taken into consideration.

322. **Insoluble residue.** The insoluble residue from the original hydrochloric acid treatment may contain barytes, magnesium silicate, silica, and clay. Ignite filter paper and residue until white, weigh as total insoluble matter; grind in agate mortar with about 10 times its weight of sodium carbonate, fuse for 1 hour in a platinum crucible, and dissolve out in hot water.

323. **Barium sulphate.** The solution from the fusion is filtered. The residue consists of barium carbonate, magnesium carbonate, etc., and is washed with hot water. The filtrate and washings are saved. Pierce filter paper and wash precipitate into clean beaker with hot dilute hydrochloric acid; finish washing with hot water, heat to boiling, add 10 c.c. of dilute sulphuric

acid to precipitate barium, filter, ignite, and weigh as barium sulphate.

324. Silica. The filtrate from the barium sulphate is added with care to the filtrate reserved in the preceding paragraph, making distinctly acid; evaporate to complete dryness, cool, add 15 c.c. of hydrochloric acid, heat to boiling, cool, settle, filter, ignite, and weigh as silica.

325. Alumina. The filtrate from the silica will contain all of the alumina except that which was dissolved in the original treatment with hydrochloric acid. This is quite constant, varying from .004 to .005 gram per gram of clay. The acid filtrates are made slightly alkaline with ammonia, and boil until odor disappears. Settle, filter, wash, ignite, and weigh as alumina.

Weight alumina $\times$ 2.5372 = weight clay.

Weight clay $\times$ .4667 = weight of silica in clay.

Any difference greater than 5 per cent may be considered as free or added silica, according to Scott.

326. Calcium and Magnesium oxides. If qualitative test shows presence of magnesium in insoluble residue from the first hydrochloric acid treatment it was present probably as magnesium silicate. Treat filtrate from the aluminum hydroxide for calcium and magnesium oxides. Magnesium silicate contains 3 to 5 per cent combined water.

327. Hydrofluoric acid treatment. Instead of resorting to fusion with sodium carbonate, the insoluble residue, which should be weighed up in a clean platinum crucible, may be treated with several drops of pure concentrated hydrofluoric acid and sulphuric acid and heated gently on a sand bath under the hood, using only sufficient heat slowly to volatilize the silica and sulphuric acid. Dissolve out in water acidulated with

hydrochloric acid. The residue, which is barium sulphate, is filtered off and estimated as such. The filtrate will contain any aluminum, calcium, and magnesium present which may be estimated and calculated as oxides as above described. The combined weight of the barium sulphate, alumina, calcium, and magnesium oxides subtracted from the weight of the insoluble residue used gives the weight of silica. This operation is much shorter than resorting to a fusion and equally as accurate.

328. Mixed carbonates and sulphates. Occasionally paints are met with which contain calcium sulphate, calcium carbonate, sulphate of lead, and white lead (basic carbonate of lead), in which case it is necessary to make a separation of the calcium compounds, which may be effected by Thompson's method as follows:

To 1 gram of the sample are added 20 c.c. of a mixture of nine parts alcohol (95 per cent) and one part of concentrated nitric acid. Stir, and allow to stand 20 minutes. Decant on a filter and repeat the treatment with the acid-alcohol mixture four times, allowing it to stand each time before decanting. The calcium carbonate will go into solution, while the calcium sulphate or gypsum remains undissolved. Add filter and contents to the residue remaining in the beaker; dissolve in hydrochloric acid with sufficient water to insure the solution of the calcium. Make alkaline with ammonia, pass in hydrogen sulphide for 10 minutes, boil, settle, filter. The filtrate and washings are concentrated to about 150 c.c. and the calcium precipitated with ammonium oxalate in the usual manner. The ignited precipitate is calculated to hydrated calcium sulphate.

329. Estimation of carbon dioxide in the presence of zinc sulphide. This method, devised by Mannhardt, is

often useful in determining complex mixtures of pigments. One gram of the pigment is ground for several minutes in a smooth glass mortar with an excess of bichromate of potash, using considerable pressure; the mixture is then placed in the carbon dioxide generator and the carbon dioxide liberated and estimated in the usual manner.

330. **Calculations.** The ignited precipitate of calcium oxide obtained from the portion insoluble in the acid-alcohol mixture is subtracted from the total calcium weighed as oxide; the remaining calcium oxide is calculated to calcium carbonate. The total carbon dioxide is determined in a portion of the sample, the portion due to the calcium carbonate is deducted from the total amount, and the remainder calculated to basic carbonate of lead. The combined sulphuric acid due to the sulphate of lime is deducted from the total combined sulphuric acid, and the remainder calculated to sulphate of lead.

Wt. calcium oxide $\times$ 3.0715 = hydrated calcium sulphate.
Wt. calcium oxide $\times$ 1.784 = calcium carbonate.
Wt. calcium carbonate $\times$ 0.440 = carbon dioxide.
Wt. carbon dioxide $\times$ 8.8068 = basic carbonate of lead.
Wt. of hydrated sulphate of lime $\times$ 0.4561 = combined sulphuric acid.
Wt. of combined sulphuric acid $\times$ 3.788 = sulphate of lead.

CHAPTER XVII.

ANALYSIS OF WHITE PAINTS (continued).

Analysis of White Paints According to Thompson.[1]

331. Schemes for the separation of the constituents from each other and into their proximate combinations depend on the constituents present, and we can treat this subject in no better way than by taking typical cases, which we now do.

332. *Sample* 1 is a mixture of barytes, white lead, and zinc oxide.

Two 1-gram portions are weighed out. One is dissolved in acetic acid and filtered, the insoluble matter ignited and weighed as barytes, the lead in the soluble portion precipitated with bichromate of potash, weighed in Gooch crucible as chromate, and calculated to white lead.

The other portion is dissolved in dilute nitric acid, sulphuric acid added in excess, evaporation carried to fumes, water added, the zinc sulphate solution filtered from barytes and lead sulphate and precipitated directly as carbonate, filtered, ignited, and weighed as oxide.

333. *Sample* 2 is a mixture of barytes and so-called sublimed white lead.

Weigh out three 1-gram portions. In one determine zinc oxide, as in case 1. Treat a second portion with boiling acetic acid, filter, determine lead in filtrate, and calculate to lead oxide. Treat third portion by boiling

[1] J. Soc. Chem. Ind., June 30, 1896.

with acid ammonium acetate, filter, ignite, and weigh residue as barytes; determine total lead in filtrate, deduct from it the lead as oxide, and calculate the remainder to sulphate. Sublimed lead contains no hydrate of lead, and its relative whiteness is probably due to the oxide of lead being combined with the sulphate as basic sulphate. Its analysis should be reported in terms of sulphate of lead, oxide of lead, and oxide of zinc.

334. *Sample* 3 is a mixture of barytes, sublimed lead, and white lead.

Determine barytes, zinc oxide, lead soluble in acetic acid and in ammonium acetate, as in case 2; also, determine carbonic acid, which calculate to white lead, deduct lead in white lead from the lead soluble in acetic acid, and calculate the remainder to lead oxide.

335. *Sample* 4 is a mixture of barytes, white lead, and carbonate of lime.

Determine barytes and lead soluble in acetic acid (white lead), as in case 1. In filtrate from lead chromate precipitate lime as oxalate, weigh as sulphate, and calculate to carbonate. Chromic acid does not interfere with the precipitation of lime as oxalate from acetic acid solution.

336. *Sample* 5 is a mixture of barytes, white lead, zinc oxide, and carbonate of lime.

Determine barytes and white lead as in case 1. Dissolve another portion in acetic acid, filter, and pass sulphureted hydrogen through the boiling solution, filter, and precipitate lime in filtrate as oxalate; dissolve mixed sulphides of lead and zinc in dilute nitric acid, evaporate to fumes with sulphuric acid, separate, and determine zinc oxide, as in case 1.

337. *Sample* 6 is a mixture of barytes, white lead, sublimed lead, and carbonate of lime.

Determine barytes, lead soluble in acetic acid and in ammonium acetate, as in case 2, lime and zinc oxide, as in case 5, and carbonic acid. Calculate lime to carbonate of lime, deduct carbonic acid in it from total carbonic acid, calculate the remainder of it to white lead, deduct lead in white lead from lead soluble in acetic acid, and calculate the remainder to oxide of lead.

338. *Sample* 7 contains as insoluble matter, barytes, china clay, and silica.

After igniting and weighing the insoluble matter, carbonate of soda is added to it and the mixture fused. The fused mass is treated with water and the insoluble portion filtered off and washed. This insoluble portion is dissolved in dilute hydrochloric acid, and the barium present precipitated with sulphuric acid in excess. The barium sulphate is filtered out, ignited, weighed, and if this weight does not differ materially — say by 2 per cent — from the weight of the total insoluble matter, the total insoluble matter is reported as barytes. If the difference is greater than this, add the filtrate from the barium sulphate precipitate to the water-soluble portion of fusion. Evaporate and determine the silica and the alumina in the regular way. Calculate the alumina to china clay on the arbitrary formula $2\,SiO_2$, Al_2O_3, $2\,H_2O$, and deduct the silica in it from the silica, reporting the latter in a free state. It is to be borne in mind that china clay gives a loss of about 13 per cent on ignition, which must be allowed for. China clay is but slightly used in white paints as compared with barytes and silica.

339. *Sample* 9 contains sulphide of zinc.

Samples of this character are usually mixtures in varying proportions of barium sulphate, sulphide of zinc, and oxide of zinc. Determine barytes as matter insoluble in nitric acid, the total zinc, as in case 1, and the zinc soluble in acetic acid, which is oxide of zinc. Calculate the zinc insoluble in acetic acid to sulphide.

340. *Sample* 10 contains sulphite of lead.

This is of rare occurrence. Sulphite of lead is insoluble in ammonium acetate, and may be filtered out and weighed as such. It is apt on exposure to the air in the moist state to become oxidized to sulphate of lead.

There are certain arbitrary positions which the chemist must take in reporting analyses of white paints:

1st. White lead is not uniformly of the composition usually given as theoretical ($2\,PbCO_3$), (PbH_2O_2), but in reporting we must accept this as the basis of calculating results, unless it is demonstrated that the composition of the white lead is very abnormal.

2d. In reporting oxide of lead present this should not be done except in the presence of sulphate of lead, and if white lead is present, then only where the oxide is more than 1 per cent; otherwise calculate all the lead soluble in acetic acid to white lead.

3d. China clay is to be calculated to the arbitrary formula given.

In outlining the above methods we have in mind many samples that we have analyzed, and the combinations we have chosen are those we have actually found present.

341. TYPICAL ANALYSES OF MIXED PAINTS.[1]

	I.	II.	III.	IV.
Color	Stone.	Lead	Gray.	White.
Can	1.00 qt.	4.06 qt.	1.06 qt.	1.08 qt.
Contents	.90 qt.	4.01 qt.	1.05 qt.	.93 qt.
Net weight	2 lbs. 14 oz.	16 lbs. 3 oz.	4 lbs.	3 lbs. 4 oz.
Vehicle	50.1	34.2	38.2	36.9
Pigment	49.9	65.8	61.8	63.1
	100.00	100.00	100.00	100.00
ANALYSIS OF VEHICLE.				
Linseed oil	68.9	90.4	90.6	89.6
Benzine drier	16.1	....	3.4	10.1
Turpentine drier.	....	9.4	4.0	....
Water	15.0	0.2	2.0	0.3
	100.00	100.00	100.00	100.00
ANALYSIS OF PIGMENT.				
White lead	21.73	49.53	16.64	21.56
Lead sulphate	0.85	0.44	13.48	1.09
Zinc oxide	47.89	49.64	39.80	49.25
Calcium carbonate.	21.98	.....	10.68	1.80
Barytes	.....	.....	18.93	.....
Silica	5.41	.....	.....	.....
Magnesium silicate,	.....	.....	.....	25.87
Color, undetermined, etc.	2.14	0.39	0.47	0.43
	100.00	100.00	100.00	100.00

[1] Analyses made by author.

342. No. I is a fair type of a large number of mixed paints, short in volume, short in weight, low in pigment, nearly one-third of the vehicle being benzine and water, and 27 per cent of total pigment inert material.

No. II is a strictly first-class paint in every respect, full measure, 16 lbs. to the gallon, pure turpentine drier, and high white lead content.

No. III is full measure and full weight. The percentage of drier is well within the usually accepted limits, but the manufacturer obtains a considerable relief by the use of nearly 30 per cent of inert pigments costing

only a small fraction of the price of white lead or zinc. This paint also has a very small percentage of added water.

No. IV is 7 per cent short in volume, is low in lead pigments, and contains nearly 28 per cent of inert pigment, which in this case is mainly magnesium silicate.

343. Calculation of the approximate cost of mixed paints using No. I and No. II as types.

COST OF VEHICLE.

Liquid.	Cost per Gallon.	No. I.		No. II.	
		Gal.	Total Cost.	Gal.	Total Cost.
Linseed oil . . .	$0.40	68.9	$27.56	90.4	$36.16
Turpentine drier .	1.00	.....	.....	9.4	9.40
Benzine drier . .	0.0326	16.1	5.25	.....	.....
Water	0.00	15.0	0.00	0.2	.....

100 gallons (750 pounds), No. I, cost $32.81.
1 pound costs $0.0438.
50.1 pounds cost $2.19.
100 gallons (750 pounds), No. II, cost $45.56.
1 pound costs $0.0607.
34.2 pounds cost $2.09.

COST OF PIGMENT.

Pigment.	Cost per Lb.	No. I.		No. II.	
		Lbs.	Total Cost.	Lbs.	Total Cost.
White lead . . .	$0.065	21.73	$1.41	49.53	$3.22
Lead sulphate[1] .	0.05	0.85	0.04	0.44	0.02
Zinc oxide . . .	0.05	47.89	2.39	49.64	2.48
Inert pigments .	0.01	27.39	0.27	.....	.....
Color	0.05	2.14	0.11	0.47	0.02

[1] Lead sulphate present in the zinc oxide.

100 pounds total pigment, No. I, cost $4.22.
1 pound costs $0.042.
49.9 pounds cost $2.11.

100 pounds total pigment, No. II, cost $5.74.
1 pound costs $0.057.
65.8 pounds cost $3.75.

No. I.

50.1 pounds liquid cost	$2.19
49.9 pounds pigment cost	2.11
100.0 pounds paint cost	$4.30
1.0 pound paint costs	0.043
1 gallon (2 pounds 14 ounces) × 4 costs	0.495

No. II.

34.2 pounds liquid cost	$2.09
65.8 pounds pigment cost	3.75
100.0 pounds paint cost	$5.84
1 pound paint costs	0.0584
1 gallon (or 16 pounds 3 ounces) costs	0.945

In other words, one paint costs almost exactly twice as much as the other, as regards paint and oil ingredients. The cost of the can (gallon size), label, and crate is about 10 cents. Salesmen's commissions, salary, and traveling expenses are about 5 cents per gallon; the cost of manufacture, depreciation of plant and machinery, 6 to 8 cents per gallon.

It must also be borne in mind that the cost of crude materials has advanced markedly during the last few years. The following table prepared by the Paint Manufacturers' Association shows the increase in cost of various paint materials in 1907 as compared with 1897:

Material.	Per cent. Increase in Cost.
White lead	61.8
Zinc oxide	40.5
Barium sulphate	44.2
Linseed oil	45.4
Turpentine	155.0
Japan drier	42.0
Tin cans	33.0
Packing boxes	64.2

344. ANALYSES OF SUBLIMED LEAD PAINTS BY AUTHOR.

	I. White.	II. White.	III. Pearl Gray.	IV. White.
Net weight, lbs. and oz. . .	15	15 : 1	14 : 8	3 : 20
Capacity of can, qts. . . .	3.96	4.00	4.00	1.03
Contents, qts.	3.95	3.94	3.86	.95
	Per cent.	Per cent.	Per cent.	Per cent.
Pigment by weight	57.0	59.2	58.6	64.8
Vehicle by weight	43.0	40.8	41.4	35.2
	100.0	100.0	100.0	100.0
ANALYSIS OF VEHICLE.				
	Per cent.	Per cent.	Per cent.	Per cent.
Linseed oil	90.5	90.4	90.4	84.5
Drier	9.3[1]	9.5	9.6	6.4
Water	0.2	0.1	0.0	9.1
	100.0	100.0	100.0	100.0
ANALYSIS OF PIGMENT.				
	Per cent.	Per cent.	Per cent.	Per cent.
White lead.	0.00	0.00	0.00	0.00
Lead sulphate[2]	58.37	33.46	35.56	59.09
Lead oxide.	5.99	9.63	8.93	16.01
Zinc oxide	35.24	56.38	55.11	5.18
Barium sulphate	0.00	0.00	0.00	19.08
Undetermined color, etc. .	0.40	0.53	0.40	0.64
	100.00	100.00	100.00	100.00

[1] Benzine. [2] Sublimed lead.

In the above analyses the percentage of zinc oxide incidental to the manufacture of sublimed lead is included in the total zinc oxide.

345. ANALYSES OF LEADED ZINC PAINTS BY AUTHOR.

	I. Lead Color.	II. White.	III. Blue.	IV. Gray.
Net weight, lbs. and oz. . .	6 : 14	3 : 8	0 : 14.5	5 : 10
Capacity of can, qts. . . .	1.91	1.06	.33	1.95
Contents, qts	1.82	1.00	.28	1.70
	Per cent.	Per cent.	Per cent.	Per cent.
Pigment by weight	58.9	60.7	57.0	57.8
Vehicle by weight	41.1	39.3	43.0	42.2
	100.0	100.0	100.0	100.0

ANALYSIS OF VEHICLE.

Linseed oil	80.2	56.9	60.4	77.6
Benzine drier	8.5	20.6	25.7	7.9
Water	11.3	22.5	13.9	14.5
	100.0	100.0	100.0	100.0

ANALYSIS OF PIGMENT.

	Per cent.	Per cent.	Per cent.	Per cent.
White lead	.....	.....	.....	.....
Lead sulphate	39.26	18.13	17.77	14.23
Zinc oxide	34.20	34.04	33.58	37.57
Calcium carbonate	5.39	41.09	39.88	41.70
Barytes	19.90	6.20	6.40	6.10
Undetermined color, etc.	1.25	0.54	2.37[1]	0.40
	100.00	100.00	100.00	100.00

346. ANALYSES BY AUTHOR OF MIXED PAINTS FOR INSIDE USE.

	I. Inside White.	II. Inside White.	III. Inside White.
Net weight, lbs. and oz.	3 : 0	15 : 0	14 : 2
Capacity of can, qts.	1.04	0.30	0.30
Contents, qts.	0.99	0.26	0.24
	Per cent.	Per cent.	Per cent.
Pigment	62.9	28.3	62.8
Vehicle	37.1	71.7	37.2
	100.0	100.0	100.0

VEHICLE.

	Per cent.	Per cent.	Per cent.
Linseed oil	60.1[2]	68.6[2]	77.9
Turpentine	39.9	30.0	22.1
Water	0.0	1.4	0.0
	100.0	100.0	100.0

PIGMENT.

	Per cent.	Per cent.	Per cent.
White lead	.....	.....	18.84
Lead sulphate	2.57	.....	.....
Zinc oxide	70.27	99.80	80.45
Lithopone	26.33	.....	.....
Barium sulphate 20.12	.....	.....	.....
Zinc sulphide 6.13	.....	.....	.....
Silica	0.28	.....	.....
Undetermined	0.55	0.20	00.71
	100.00	100.00	100.00

[1] Color largely organic.

[2] Includes a small amount of dammar varnish.

347. ANALYSES OF CHEAPENED MIXED PAINTS BY THE AUTHOR.

Showing the various devices used for cheapening the cost of production, — short volume, low pigment content, practical absence of all lead pigments, excessive use of drier, high per cent of water and of cheap inert pigments. Two of these brands were sold as straight white lead and zinc oxide paints.

	I. White.	II. Gray.	III. Lead Color.	IV. Slate Color.
Net weight, lbs. and oz.	3:0	6:3	9:9	5:12
Capacity of can, qts.	1.03	1.95	3.37	1.90
Contents, qts.	.99	1.92	2.42	1.85
	Per cent.	Per cent.	Per cent.	Per cent.
Pigment by weight	55.1	54.6	67.10	50.8
Vehicle	44.9	45.4	32.90	49.2
	100.0	100.0	100.0	100.0

ANALYSIS OF VEHICLE.

	Per cent.	Per cent.	Per cent.	Per cent.
Linseed oil	72.5	54.4 [1]	83.9 [1]	61.9
Benzine drier	9.1	28.9	4.3	22.0
Water	18.4	16.7	11.8	16.1
	100.0	100.0	100.0	100.0

ANALYSIS OF PIGMENT.

	Per cent.	Per cent.	Per cent.	Per cent.
White lead	.....	.....	.....	.....
Lead sulphate	.89	3.11	4.73	0.74
Zinc oxide	53.86	24.67	24.34	60.10
Calcium carbonate	43.39	40.07	4.47	21.11
Magnesium carbonate	0.73	.....	.....	.....
Barytes	.....	22.10	66.26	.....
Silica	0.60	7.26	.....	16.25
Undetermined color, etc	.53	2.79	0.20	1.80
	100.00	100.00	100.00	100.00

[1] Very low-grade linseed oil.

CHAPTER XVIII.

KALSOMINE, COLD-WATER PAINTS, AND FLAT WALL FINISHES.

348. Kalsomine. Kalsomines may be divided into two classes, — those which require hot water to develop their adhesive strength and those which may be mixed with cold water, the glue having been so treated as to be soluble in cold water. Kalsomines of the latter class are more convenient to use but more difficult to manufacture. Either class, however, consists essentially of glue and one or more of the following inerts, whiting, china clay, gypsum, magnesium silicate, together with the necessary tinting colors.

349. The essential qualities of a good kalsomine are:

1. Ease of preparation with water, with quick development of adhesive strength.
2. Opacity and freedom from chalking.
3. Absence of brush marks and lap streaks on application.
4. Maintenance of "sweetness" for at least 3 days after having been mixed with water.
5. Permanence of tints.

350. Whiting is undoubtedly the best white base for kalsomine, as it possesses the greatest body, the other three inerts being more transparent, but spread easier under the brush, so that the majority of kalsomines contain besides the whiting a percentage varying from 20 to 40 of these other inerts. Chalking is caused by using an insufficient amount of glue or having weakened

the strength of the glue by the excessive use of preservatives, a certain amount of which must be used in order to maintain the "sweetness" for several days after a batch has been mixed with water, as the price at which kalsomine is sold precludes the use of high-priced glues. The best and most generally used preservatives are aluminum sulphate and zinc sulphate, and, as above stated, their excessive use weakens the glue. When mixed with water, a kalsomine should "jell" properly, and when applied on a wall the edges of the first section should not dry before the next section is started, else the lap will show. The retarding of the drying of a kalsomine can be accomplished by the use of Irish moss.

351. Permanence of tints is secured by avoiding colors which are affected by the alkali action of the lime in the plaster, especially Prussian or Chinese blue and chrome green, using in their place, as much as possible, blue and green lakes, which are known as "lime proof." The various yellows are obtained by the acid of ocher and the chrome yellows; the reds with the iron oxide pigments, para reds precipitated on an inert base and to some extent other organic reds; the greens with lime-proof green lakes and chrome greens, although the latter are not permanent; the blues are lime-proof blue lakes and ultramarine blue. The intermediate colors are obtained by intermixing the above and with the aid of the siennas, umbers, and blacks.

352. **Analysis.** The analysis of kalsomines offers no particular difficulties, the percentage of glue being obtained by running a nitrogen determination by the Kjeldahl method and multiplying by the factor 0.37. Zinc sulphate and aluminum sulphate are detected and estimated in the usual manner; the white base and

tinting colors by the usual analytical methods, the percentage of lake colors being obtained by difference.

353. The following analyses made by the author are representative of several of the leading combinations on the market:

	I. White. Per cent.	II. White. Per cent.
Whiting	63.7	68.2
China clay	16.3	9.1
Gypsum	10.1	15.5
Glue	5.5	4.0
Aluminum sulphate	1.4	2.1
Moisture	2.5	0.4
Ultramarine blue	trace	.....
Undetermined	0.5	0.7
	100.0	100.0

	Yellow Tint. Per cent.
Whiting	60.1
China clay	15.0
Gypsum	11.3
Ocher	2.4
Lead chromate	2.4
Moisture	1.9
Glue	5.1
Alum sulphate	0.9
	100.0

	Solid Wall Red. Per cent.
Clay	22.2
Red lake	9.4
Barium sulphate	63.1
Glue	4.9
Moisture	0.4
	100.0

354. **Lakes.** The lime-proof lakes used are usually on a barium carbonate or sulphate base, less commonly on a silica or silicate base, and this base in the case of solid wall colors, so-called, will constitute the larger portion of the kalsomine.

355. **Testing.** Hot-water kalsomines are prepared by simply grinding together the glue, white base, and tinting colors, after mixing in a high-speed rotary mill. In the manufacture of the cold-water kalsomines the glue is given a special treatment to render it soluble in cold water before it is incorporated with the pigments, the mixing and grinding being accomplished in the usual manner. The testing of the glue for strength and sweetness is a most important consideration, especially in the manufacture of cold-water kalsomines. The method adopted by the author is to prepare a small batch of kalsomine according to the regular formula, incorporating the ingredients in the mixer and grinding in the mill in the usual manner, the glue, however, being the one item omitted completely, and the base so obtained is kept in the laboratory for testing purposes. The weighed sample of the glue which has been melted in the calculated amount of hot water is cooled to room temperature and the requisite amount of kalsomine base added, care being taken to obtain a mix free from lumps. A portion is brushed out uniformly on a sheet of unglazed paper, allowed to dry, and the adhesiveness noted by rubbing and by the folding of the paper. The remainder is allowed to stand loosely covered in the laboratory for 3 days, it then being stirred up and the "sweetness" noted. It is a peculiar fact that a glue which when melted up in water and allowed to jell will keep sweet by itself for 3 days may undergo marked decomposition in 36 hours when incorporated with the pigment portion of the kalsomine. Usually the deep tints and solid wall colors will not require the addition of a glue preservative, as the tinting colors themselves will prevent the decomposition of the glue.

356. Cold-water paints. The paints which come under this head are prepared very much like kalsomine except that the binding agent instead of glue is casein, together with sodium carbonate or quicklime or both, which are added in the dry form, the combination with the casein being affected on the addition of water when being prepared for use. The tints are usually restricted to those obtained with ochre, blacks, and cheap Venetian reds. Unless kept in a tight package cold-water paints will lose their strength, as the quicklime will absorb carbon dioxide from the air, becoming inert. Caustic soda is sometimes used, but possesses marked disadvantages.

357. Analyses. The following analyses by the author afford some idea of the composition of this class of paints:

	I. Outside White. Per cent.	II. Inside White. Per cent.
Whiting	55.55	60.60
Clay	13.90	14.12
Calcium sulphate	13.65	16.08
Casein	9.03	6.05
Calcium oxide	4.72	1.51
Sodium hydroxide	.....	.....
Sodium carbonate	3.15	1.64
Ultramarine blue	trace	.....
	100.00	100.00

358. Specifications for Cold-Water Paint, Navy Department, 1908.

1. Cold-water paint shall consist of whiting, 20 to 25 per cent silicious matter, free lime equivalent to from 5 to 10 per cent of calcium hydrate, $Ca(OH)_2$, and from 10 to 12 per cent of casein, with not more than traces of calcium sulphate and small amounts of zinc oxide.

2. It must be capable of readily remixing at the end of fifteen hours after having been mixed in proper pro-

portions with cold water, and must not possess an offensive odor.

3. When dry the paint must be of white color, and not chip, scale, powder, or rub off when washed with cold water, and in these regards must be equal to standard sample.

359. Flat wall finishes. During the last few years there has been developed a demand for a flat wall finish similar to that produced by kalsomine, but capable of being washed and cleaned and not affected by moisture.

360. The pigments used for this purpose must have a high degree of opacity, lithopone perhaps being the one most used for the white and as a base for the tints, although Paris white and gypsum may replace the lithopone in some of the tints, especially the yellows and greens. The most permanent blues are obtained with ultramarine; lime-proof reds are used where possible; and the yellow tints are produced with chrome yellow and to some extent with ocher.

361. The ratio of vehicle to pigment is much the same as in ordinary mixed paints. The desired flat effect is obtained by the use of a large percentage of volatile thinners, which will constitute about 75 per cent of the vehicle. The volatile thinners used may be a mixture of turpentine and benzine, or turpentine and petroleum spirits, or petroleum spirits only.

362. The remaining portion of the vehicle, which is just sufficient in quantity to act as a binder for the pigment, may be a special varnish or a mixture of boiled oil and a varnish, such as a linseed oil-rosin varnish.

363. Analyses. The following analyses are typical of this class of finishes:

	White. Per cent.	Yellow. Per cent.
Lithopone	68.4	12.1
Gypsum	....	24.0
Chrome yellow	....	23.9
Petroleum thinner	23.5	29.7
Linseed oil and varnish	8.1	10.3
	100.0	100.0

CHAPTER XIX.

COMPOSITION OF COLORED PAINTS.

364. Lack of uniformity. After the extraction of the vehicle it is necessary to examine the pigment qualitatively in order to ascertain the ingredients to be determined. The usual qualitative scheme may be followed with advantage. The colors, as given on the color cards of paint manufacturers, are usually confined to a limited number of combinations, the possible components of which may be easily ascertained, and which, in fact, are usually well known to paint chemists; but to the chemist who has had but little experience along paint lines, the following tables of color ingredients will be of interest. Unfortunately, manufacturers are not agreed among themselves as to standards for naming colors; for example, a tea green put up by one manufacturer may not correspond with a tea green put up by another; but, by a careful study of the color cards issued by reputable paint manufacturers, it is usually possible to identify the color to be analyzed. Also the same or nearly the same color may be produced by different combinations of color pigments, hence it is necessary to state all of the possible constituents that may be used, as far as the author has been able to ascertain them, even though it is quite probable that they may not all be present in the same paint.

365. Reds:

Brick. Base white, ochre and Venetian red.

Flesh Color. Base white, ochre, Venetian red, and sometimes orange chrome yellow.

Indian Red. Indian red.

Lilac. Ultramarine, carmine, Indian red, ochre, lampblack.

Maroon. Carmine, ultramarine, lampblack, Tuscan red.

Pink. Base white, orange chrome yellow.

Terra Cotta. Base white, burnt sienna, umber, chrome yellow, Venetian red, ochre.

Salmon. Base white, vermilion, lemon chrome yellow, sienna, ochre, Venetian red, orange mineral.

Tuscan Red. Tuscan red, Indian red, Para vermilions.

Venetian Pink. Base white, Venetian red.

Venetian Red. Venetian red.

366. Blues:

Azure Blue. Base white, ultramarine blue, chrome green, Prussian blue.

Bronze Blue. Black, Prussian blue.

Dark Blue. Base white, chrome green, Prussian blue, ultramarine, black.

Light Blue. Base white, ultramarine, Prussian blue.

Neutral Blue. Base white, Prussian blue, umber, black.

Robin's Egg Blue. Base white, ultramarine, lemon chrome green.

Sky Blue. Base white, cobalt blue, Prussian blue, ultramarine blue, chrome yellow.

367. Yellows:

Buff. Base white, ochre, black, red chrome lead.

Canary. Base white, lemon chrome yellow, chrome green.

Citron. Base white, Venetian red, Prussian blue, chrome yellow.

Cream. Base white, ochre, Venetian red.
Deep Cream. White, ochre, Venetian red.
Ecru. Base white, ochre, chrome yellow, black, chrome green.
Ivory. Base white, chrome yellow, ochre.
Lemon. Base white, chrome yellow.
Manilla. Base white, ochre, chrome yellow.
Stone. Base white, ochre, umber, chrome yellow.
Straw. Base white, chrome yellow, ochre, Venetian red.

368. Greens:

Ivy Green. Ochre, lampblack, Prussian blue.
Light Green. White, Prussian blue, chrome green.
Manse Green. Chrome green, chrome yellow, ochre.
Moss Green. Base white, ochre, chrome green, lampblack.
Olive Green. Lemon chrome yellow, ochre, ultramarine blue, Prussian blue, Indian red, chrome green, lampblack.
Pea Green. Base white, chrome green, very rarely emerald green.
Sap Green. Base white, chrome yellow, lampblack, chrome green.
Sea Green. Base white, chrome green, sienna, ochre.
Tea Green. Base white, chrome green, chrome yellow, lampblack.
Willow Green. Base white, chrome green, umber, ivory, black.

369. Browns:

Acorn Brown. Sienna, carmine, Indian red, lampblack, ochre.
Brown. Indian red, lampblack, ochre.

Chocolate. Similar to acorn brown.

Cork Color. Base white, ochre, Indian red, lampblack, umber.

Dark Drab. Base white, Indian red, lampblack, Prussian blue, yellow ochre.

Doe Color. Base white, sienna, umber, ochre, lampblack.

Dove Color. Base white, Prussian blue, lampblack, ochre, Indian red, umber, sienna.

Drab. Base white, umber, Venetian red, yellow ochre, black.

Fawn. Base white, ochre, Indian red, lampblack, sienna, umber, chrome yellow, Venetian red.

Lava. Base white, black, chrome orange, chrome yellow.

Sandstone. Umber.

Snuff Brown. Base white, ochre, Indian red, Venetian red.

370. Greys and grays:[1]

Ash Gray. Base white, ochre, lampblack, sienna, ultramarine blue.

Dark Slate. Base white, Prussian blue, lampblack.

French Gray. Base white, black, ultramarine Prussian blue, Venetian red.

Granite. Base white, ochre, lampblack.

Graystone. Base white, black, Prussian blue, ultramarine, Venetian red.

Lead. Base white, lampblack, Prussian blue.

Light Grey. Base white, lampblack, Prussian blue.

[1] Grey is understood to mean an admixture of black and white, while gray is an admixture of black and white to which another color has been added, provided, of course, that the black and white predominate.

Pearl. Similar to French gray.

Silver Gray. Base white, ochre, lampblack, chrome yellow.

Smoke Gray. Base white, ochre, lampblack.

Steel Gray. Base white, chrome yellow, lampblack.

Stone Gray. Base white, chrome yellow, black.

Warm Gray. Base white, ochre, lampblack, sienna, Prussian blue.

CHAPTER XX.

ANALYSIS OF INDIAN REDS, VENETIAN REDS, TUSCAN REDS, RED OXIDES, AND OCHRES.

371. **Hygroscopic moisture.** Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

372. **Combined water, etc.** Transfer above sample to a weighed platinum crucible and heat for one hour over an ordinary lamp, or better in a muffle. Loss in weight indicates amount of combined water. Carbonates and organic matter render the results inaccurate, in which case continue the ignition at bright red heat for several hours, and weigh again. Determine the carbon dioxide in another portion of the sample and estimate the combined water by difference. If a large amount of calcium sulphate is present, it is possible to heat it strongly enough to partially drive off the combined sulphuric acid, and unless this be taken account of the analysis will total up to more than 100 per cent. In the case of a Tuscan red which has precipitated upon it an organic color, the loss in weight is best reported as combined water and organic matter. The presence of an organic color may always be detected by the characteristic odor given off at the beginning of the ignition.

373. **Silica and barium sulphate.** One gram of the pigment is intimately mixed with 6 to 8 grams of potassium bisulphate and fused in a large porcelain crucible, the cover of which is small enough to set inside the top of the crucible, at not too high a temperature for one-

half hour, finally heating the side of the crucible to finish the conversion of any material adhering to the cover and upper portion of the crucible. The iron, aluminum, calcium, and magnesium are converted into sulphates, the barytes remains unchanged and the silica is completely dehydrated. With a little care, using a low heat at first, the fusion may be conducted with very little frothing or spattering. Fusion with bisulphate is to be preferred to solution with hydrochloric acid, as ferric chloride is appreciably volatile on boiling. Also the silicates of iron that are present in small quantity in the natural oxides are not decomposable with hydrochloric acid.

After cooling, the entire contents of the crucible may be shaken loose and dissolved in sufficient water and a little hydrochloric acid. Filter and make up to 250 c.c. unless calcium is present in large amount, in which case make up to a volume of not less than 500 c.c., as calcium sulphate is but sparingly soluble.

The residue remaining on the filter is ignited and weighed in a platinum crucible. The residue is tested for barium sulphate by the flame test: if absent the residue is reported as silica; if present the residue is treated in the crucible with hydrofluoric acid until a thin paste is formed. The mixture is stirred with a platinum wire and digested at a gentle heat; finally two or three drops of sulphuric acid are added, and the temperature gradually raised until no further loss in weight takes place, indicating that the silica has been completely expelled. The residue is weighed as barium sulphate, and the loss in weight represents the silica, or the residue of barium sulphate and silica may be fused with sodium carbonate as described under the analysis of white pigments.

374. **Ferric oxide.** An aliquot portion of the solution from 373 is heated to boiling and stannous chloride solution added cautiously until the yellow color has disappeared, and then a slight excess added. All at once, with vigorous shaking of the flask, 50 c.c. of mercuric chloride solution is added, then 50 c.c. of the manganous sulphate solution. Dilute with cold freshboiled water and titrate with permanganate solution. Calculate iron found to ferric oxide.

375. **Preparation of reagents.**

a. Stannous chloride. Dissolve 30 grams of tin in 250 c.c. of hydrochloric acid, filter through glass wool, and make up to one litre.

b. Mercuric chloride. Dissolve 50 grams in one litre.

c. Manganous sulphate. One litre should contain 66.7 grams of crystallized manganous sulphate, 333 c.c. phosphoric acid (sp. gr. 1.3), and 133 c.c. of conc. sulphuric acid.

d. Potassium permanganate. Dissolve 3.16 grams in one litre; standardize against the standard iron solution.

e. Standard iron solution. Dissolve 7.03 grams iron wire, 99.7 per cent purity, in dilute hydrochloric acid; make to one litre.

1 c.c. = 0.01 g. ferric oxide or 0.007 gr. iron.

In many cases where a rapid commercial determination of the iron content alone is desired, the pigment may be dissolved in hydrochloric acid, with the subsequent addition of a few drops of nitric acid, filtered, the iron and alumina precipitated with ammonia; after thorough washing dissolved in sulphuric acid, run through a "reductor," such as may be obtained from any of the leading supply houses, and then simply titrated with standard permanganate solution in the usual manner.

376. **Alumina.** An aliquot part of the solution in 373 is made just alkaline with ammonia, boiled, decanted, filtered, washed, redissolved, reprecipitated, filtered, ignited, and weighed as alumina and ferric oxide, the alumina being obtained by difference.

377. **Calcium.** The filtrate from the iron and alumina is treated with ammonium oxalate (50 c.c. is sufficient for 1 gram of calcium pigment). Set aside in a warm place for two or three hours, filter, ignite, and weigh as calcium oxide, or titrate with standard permanganate, as may be desired. The calcium may have been present as carbonate or sulphate or both. Hence an estimation of the sulphur trioxide present in the original sample is necessary. For this purpose 1 gram is dissolved in 30 c.c. of strong hydrochloric acid, boiled 10 minutes, diluted with 50 c.c. of water, heated to boiling, filtered, and washed with hot water. Neutralize the filtrate with ammonia, then make just distinctly acid with hydrochloric acid, boil, add 10 c.c. of barium chloride solution, continue boiling for 10 minutes, filter, wash, ignite, and weigh as barium sulphate. Calculate sulphur trioxide by multiplying weight of precipitate by 0.343.

Calculate the sulphur trioxide found to calcium sulphate and the remaining calcium to oxide, provided that the carbon dioxide is included under loss on ignition. If desired, the remaining calcium may be calculated to calcium carbonate, the combined carbon dioxide being deducted from the loss on ignition.

378. **Magnesium.** If a considerable percentage of calcium is found, magnesium is liable to be present; precipitate with sodium hydrogen phosphate in usual manner. Calculate the pyrophosphate to oxide by multiplying by the factor 0.3624.

379. ANALYSES OF INDIAN REDS, RED OXIDES, AND VENETIAN REDS.[1]

	Insoluble.	Ferric Oxide.	Alumina.	Calcium Oxide.	Carbon Dioxide.	Magnesium Oxide.	Sulphur Trioxide.	Moisture.	Loss on Ignition.
Pure Indian Red	0.67	94.35	2.69	...	...	...	...	0.20	1.53
Pure Indian Red	0.48	96.93	1.10	...	...	...	...	0.41	0.90
Pure Indian Red	0.61	97.49	0.77	...	...	...	...	0.36	0.80
Superfine Indian Red	0.65	95.05	3.96	...	...	...	...	0.06	0.19
Imported Red Oxide	19.42	77.93	0.25	1.21	...	...	...	0.20	1.41
Ordinary Red Oxide	10.82	38.30	5.43	17.99	1.32	0.96	19.20	2.50	3.45
Red Oxide	11.55	53.95	12.03	9.33	...	0.68	1.55	0.01	10.95
Red Oxide	0.71	94.88	3.20	...	...	...	...	0.15	1.98
Red Oxide	13.61	70.15	2.09	6.12	1.45	...	5.85	0.13	1.23
Imported Red Oxide	1.33	29.22	1.76	23.19	...	0.30	37.00	5.47	2.52
Best Tuscan Red Oxide	0.64	59.09	1.20	15.27	...	0.40	23.15	0.01	0.81
Turkey Red Oxide	1.90	51.97	2.31	14.85	...	0.52	17.92	6.36	4.34
Turkey Red Oxide	15.74	64.00	6.15	5.88	...	0.48	0.20	0.06	7.25
American Venetian Red	55.92	35.64	1.71	2.90	...	...	...	0.44	3.94
American Venetian Red	20.36	16.78	2.35	18.66	27.19	12.06	2.45	0.10	...
Royal Venetian Red	1.82	9.00	0.57	30.47	39.40	18.26	...	0.30	...
Royal Venetian Red	2.10	20.83	2.42	31.65	7.22	1.34	28.70	3.50	2.79
Superfine Venetian Red	18.75	76.31	2.11	0.65	0.45	...	...	0.05	1.74
Light Brilliant Venetian Red	6.06	11.56	1.01	25.46	1.65	1.88	35.15	12.12	5.30
Imported Venetian Red	27.30	61.01	6.38	0.88	...	...	2.05	0.09	2.03
Venetian Red	1.07	9.50	0.28	45.00	12.06	0.50	25.00	6.84	...
Light Victoria Venetian Red	1.46	22.79	1.19	27.95	...	0.79	36.15	6.72	3.76
Windsor Venetian Red	18.85	24.43	1.84	26.89	13.14	1.33	11.15	2.17	...
V. C. Eng. Venetian Red	2.85	18.79	3.38	39.21	18.39	0.52	16.30	0.01	...
Home Imported Venetian Red	10.81	18.78	2.05	28.50	1.78	1.36	22.67	10.68	3.95
Cutter's English Venetian Red	0.30	22.00	1.79	29.03	...	...	34.90	7.51	3.44

[1] Weems, Iowa, Eng. Soc., Jan., 1901.

380. **Tuscan reds** should contain about 60 per cent ferric oxide, and are often brightened up by having precipitated on them an organic red. Another class of oxides, carrying about the same amount of iron oxide as Tuscan reds, is "Prince's metallic." The variation of iron content is shown in the following analyses:

No.	Ferric Oxide.
I	44.07
II	38.17
III	68.45
IV	49.58
V	39.35

A complete analysis gave the following:

	Per cent.
Volatile	3.33
Ferric oxide	40.91
Alumina	3.49
Calcium oxide	2.00
Insoluble	49.57
Undetermined	0.70
	100.00

381. **Ochres,** of which the French ochres are considered the best, to pass inspection by the various service department scientists of the United States Government, must be of good bright color, contain at least 20 per cent sesquioxide of iron and not over 5 per cent of lime in any form. A good grade of yellow ochre to pass this inspection would analyze about as follows:

	Per cent.
Silica	52.14
Alumina	12.89
Ferric oxide	22.42
Calcium oxide	0.36
Combined water	10.16
Hygroscopic water	2.03
	100.00

382. ANALYSES OF OCHRES AND IRON OXIDE PIGMENTS BY THE AUTHOR.

	Moisture.	Comb. H_2O and Loss on Ignition.	Silica.	Ferric Oxide.	Alumina.	Calcium Oxide.	Magnesium Oxide.	Carbon Dioxide.	Sulphur Trioxide.	Barium Sulphate.	Undetermined.
Ochre B. F.	0.29	6.78	61.49	18.15	12.78	0.20	...	...	...	...	0.31
Ochre Clair	0.19	9.54	53.80	21.05	14.35	0.67	...	...	...	...	0.40
Ochre	0.18	8.70	52.63	23.01	15.34	...	...	...	...	...	0.14
Ochre	0.09	9.44	52.34	21.01	16.93	...	...	...	...	...	0.19
Ochre	0.85	6.60	62.00	24.96	5.29	...	...	...	...	...	0.30
Ochre J. F. L. S.	0.30	8.71	53.09	26.30	11.31	...	...	...	...	...	0.29
Ochre J. B. N. Y.	0.70	14.41	50.00	19.85	15.23	0.57	0.01	...	...	...	0.23
Venetian Red Med.	6.34	...	2.38	22.40	1.72	29.32	0.17	4.72	32.66	...	0.29
Venetian Red Med.	10.18	4.86	1.45	11.88	1.10	30.49	0.02	6.32	32.54	...	0.16
Tuscan Red	0.06	...	38.38	25.08	...	20.87	...	14.78	...	...	0.83[1]
Tuscan Red	1.32	6.08	1.51	23.30	9.55	...	...	...	...	58.24	...
Tuscan Red	0.31	...	2.22	49.55	4.61	23.78	...	18.70	0.49	...	0.34
Oxide N	0.05	3.03	8.25	85.82	1.99	...	...	...	...	...	0.83
Red Oxide	0.01	0.23	46.30	39.72	11.28	0.99	1.24	...	...	...	0.23
Indian Red	0.13	1.24	1.14	94.61	2.65	...	...	...	...	...	0.23

[1] Includes organic color.

Specifications for Venetian Red.

(Bureau of Supplies and Accounts, Navy Department, 1902.)

383. **Red, Venetian.** I. Red, Venetian (bright). The dry pigment must contain at least 20 per cent of sesquioxide of iron, not more than 15 per cent of silica, the balance to consist of sulphate of lime that has been fully dehydrated by dead burning, and rendered incapable of taking up water of crystallization.

II. Red, Venetian (deep). The dry pigment must contain at least 30 per cent of sesquioxide of iron, not more than 15 per cent of silica, the balance to consist of sulphate of lime that has been fully dehydrated by dead burning and rendered incapable of taking up water of crystallization.

III. Red, Venetian (medium). The dry pigment must contain at least 40 per cent of sesquioxide of iron, not more than 15 per cent of silica, the balance to consist of sulphate of lime that has been fully dehydrated by dead burning and rendered incapable of taking up water of crystallization.

384. **Priming ochres.** A few years ago the adulteration of priming ochres, so called, was exceedingly widespread. Paint legislation has done much to check this evil, and in such states as require the label to show the ingredients and percentages thereof, the sale of this class of goods has largely diminished, and the author believes very few property owners would care to use the cheap combination priming ochres with which the market is flooded. It is just as useless to expect the coats of paint applied over such primers to give a satisfactory service value as it is to expect a house to stand, built on a foundation of rubbish.

385. Analysis. The analysis of this class of goods may be performed substantially as described in this chapter. The vehicle should receive careful examination, as these so-called ochres are often ground in paraffin oil, low-grade linseed oil containing large quantities of foots, or in soya-bean oil. The names under which such goods are placed on the market are also misleading, as *white ochre*, *stone ochre*, etc. The nature of some of these products is indicated by the following analyses:

	I. Per cent.	II. Per cent.
Barium sulphate	36.24	62.77
Calcium carbonate	47.79	8.68
Aluminum silicate and silica	3.87	12.56 [1]
Iron oxide	...	3.14 [1]
Linseed oil	12.10	11.35
Naphtha	...	1.50
	100.00	100.00

[1] Ochre.

386. Tinting ochres. Under this head are included pure French ochres ground in linseed oil, ochres which have precipitated on them a small percentage of chrome yellow, and various mixtures of ochre, chrome yellow and inert pigments like barytes, white mineral primer, etc. When toned up with chrome yellow, these various combinations are sold under some such name as *golden ochre*, *topaz ochre*, etc. The following analyses calculated to formula indicate the nature of some of these combinations:

	I. Per cent.	II. Per cent.
Ochre	63.58	40.60
Chrome yellow	2.13	8.91
Barytes	...	7.69
Gypsum	34.29	...
Calcium carbonate	...	42.80
	100.00	100.00

387. **Domestic ochres.** It has been stated that the use of cheap domestic ochres, of low tinting strength, furnished a ready means of cheapening mixed paints in which yellow tinting colors were required, by the introduction of a large amount of inert material along with the color. This condition of affairs the author believes to be very improbable, as the color value of the domestic ochres is very unlike the accepted grades of French ochres, in that they do not produce clean, clear tints or give pleasing effects, and therefore the bother and trouble in handling domestic ochres is of greater moment than the difference in price.

CHAPTER XXI.

ANALYSIS OF BLACK PIGMENTS AND PAINTS.

388. Composition. The ordinary black pigments — lampblack, vegetable black, bone black, ivory drop black, gas black, graphite, etc. — contain carbon as their essential constituent, and while all of these products are said to be of a black color, they vary greatly in shade and still more so in tinting strength.

1. Lampblack and vegetable black are essentially soot blacks, being the soot deposited from the combustion of oily bodies such as dead oil. Lampblack has a distinct gray tint, as may be shown by comparison with ivory black. These blacks are apt to contain varying quantities of oil, owing to the nature of their manufacture; less than 1 per cent of oil often being sufficient to retard seriously the drying of lampblack paints. Vegetable blacks are more voluminous than lampblacks and are usually of a jet black color.

2. Carbon black is usually produced from the incomplete combustion of natural gas. While its tinting power is very great, its use has been largely abandoned owing to its tendency to produce a streaky color when used in tinting paints.

3. Bone black is, as its name indicates, obtained by the charring of bones in retorts. The carbon content varies usually between 12 and 22 per cent, the balance consisting of moisture, phosphate of calcium, and carbonate of calcium. The best grades of bone black are made from selected sheep bones. An exceedingly

intense black is made by digesting selected bones in hydrochloric acid until all of the mineral matter is dissolved, leaving the carbon in a flocculent state. This black is often sold under the name of black toner, and is one of the highest priced blacks.

4. Animal black is a name sometimes given to bone black but is also used to designate a wide variety of blacks prepared in the same way as bone black from waste animal products of all kinds, as leather scrap parings, horn trimmings, etc.

5. Frankfort black, drop black, and German black are terms used to designate blacks made from a variety of organic materials, such as vine twigs, refuse of wine making, peach stones, bone shavings, etc. These blacks vary in hue from a bluish black to a reddish black.

6. Graphite, while not used to any extent in house paints, is largely used in bridge, elevator, and warehouse paints. It is rarely used by itself for these purposes, silica, calcium carbonate and iron oxide pigments, zinc and lead being the other usual constituents. It may be tested qualitatively in the extracted pigment by rubbing a portion of the sample between the palms, which soon assume the characteristic appearance produced by stove polish. Of all the black pigments graphite alone gives this test.

7. Charcoal black and vine black are produced by the charring of wood products, and contain besides carbon the ash ingredients common to wood. Charcoal blacks are usually made from maple, willow, and basswood, and vine blacks from the charring of the grapevine. Paints containing considerable quantities of these blacks are liable to saponify badly owing to the moisture and potash salts present.

8. Mineral black, which is still occasionally used, is black slate finely ground.

389. **Moisture.** Dry 2 grams at 105° C. for 3 hours. Loss in weight represents approximately the amount of moisture present.

390. **Oils.** Extract 2 grams with ether in a fat extraction apparatus. After removing the ether and drying, any increase in weight represents the amount of oily matter present.

391. **Ash.** Two grams are weighed into a crucible and heated over a Bunsen burner until all the carbon is burned off. If the ash constitutes only a small per cent, it may be cooled and weighed directly. Otherwise the residue is moistened with a solution of ammonium carbonate, heated gently, and weighed. The object of this operation is to restore the carbon dioxide which may have been expelled from the bases by the strong heat to which they have been subjected.

392. **Carbon.** The carbon is usually estimated by difference, by adding together the moisture, oil, and ash, and subtracting from 100.

393. **Calcium.** Digest the residue from 391 in a mixture of 25 c.c. of concentrated hydrochloric acid and 5 c.c. of concentrated nitric acid on the hot plate for one-half hour, dilute, filter, and make up to 250 c.c. in a graduated flask. Any appreciable residue on the filter may indicate addition of barytes, silica, clay, or alumina. Determine the calcium and magnesium in an aliquot portion of the solution by adding ammonia in small quantities until a precipitate is formed, then acetic acid in excess until redissolved, except for traces of iron which may be removed by filtration. Ammonium oxalate is added, and the calcium precipitate treated in the usual manner.

394. Phosphoric acid. Take an aliquot portion of the solution prepared above, neutralize with ammonia, and clear with a few drops of nitric acid, add about 5 grams of dry ammonium nitrate or a solution containing that amount. To the hot solution add 50 c.c. of molybdic solution for every decigram of phosphoric acid that is present. Digest at about 65° for an hour, filter, and wash with cold water, or preferably ammonium nitrate solution. Test the filtrate for phosphoric acid by renewed digestion and addition of more molybdic solution. Dissolve the precipitate on the filter with ammonia and hot water, and wash into a beaker to a bulk of not more than 100 c.c. Nearly neutralize with hydrochloric acid, and add magnesia mixture from a burette; add slowly (about 1 drop per second), stirring vigorously. After 15 minutes add 30 c.c. of ammonia solution of density 0.96. Let stand for some time; 2 hours is usually enough. Filter, wash with 2.5 per cent ammonia, ignite to whiteness or to a grayish white, and weigh as magnesium pyrophosphate.

395. Preparation of reagents. *Molybdic solution.* Dissolve 100 grams of molybdic acid in 400 grams or 417 c.c. of ammonia, specific gravity 0.96, and pour the solution thus obtained into 1500 grams or 1250 c.c. of nitric acid, specific gravity 1.20. Keep the mixture in a warm place for several days, or until a portion heated to 40° deposits no yellow precipitate. Decant the solution from any sediment and preserve it in glass-stoppered vessels.

Magnesia Mixture. Dissolve 110 grams of crystallized magnesium chloride, 280 grams of ammonium chloride, in 700 c.c. of ammonia of specific gravity 0.96, and sufficient water to make 2000 c.c.

396. Magnesium. The filtrate, from which the cal-

cium has been precipitated, is evaporated to a small bulk and made alkaline with ammonia. After standing several hours the magnesium precipitate is filtered, ignited, and weighed, and calculated to magnesium by multiplying by 21.88.

397. Calculations. The magnesium is calculated to magnesium phosphate, and the remainder of the phosphoric acid to calcium phosphate. Any calcium remaining is calculated to calcium carbonate.

Genuine ivory black, made by carbonizing waste fragments and turnings of ivory, is often adulterated with bone black, which is somewhat similar in composition, but contains only a small amount of magnesium phosphate as compared with the ivory black.

398. Specifications for drop black. (Navy Department, May, 1903.) Drop black must be of good deep luster and consist of calcined bone black only. The addition of blue or gas carbon black will be ground for rejection. The paste must contain not less than 45 per cent of pure pigment.

The pigment must be of the best quality, free from all adulterants, and equal in all respects to the standard sample.

The paste must be ground in pure raw linseed oil only, to a medium stiff paste, which will break up readily in thinning.

399. Specifications for carbon black, etc. (Treasury Department, 1907.) Carbon black must be pure gas carbon with not more than 0.5 per cent of ash, that is, 97.5 per cent of pure carbon and the balance moisture, ash, etc.

Hard black; should be suitable for making the highest class of plate printing inks; and other factors being equal, a color having chemical and physical properties

adapted for that purpose and which produces an ink having the most satisfactory working qualities will be selected. The black now in use has the following chemical analysis:

	Per cent.
Ash	48.3
Moisture	3.7
Carbon	48.0

Ash insoluble in hydrochloric acid 11.4 per cent.

Soft Black. Requirements same as for hard black. The black in use has the following chemical analysis:

	Per cent.
Ash	56.1
Moisture	2.5
Carbon (by diff.)	41.4
	100.0

Ash insoluble in hydrochloric acid 36.3 per cent.

400. COMPOSITION OF IVORY AND BONE.

IVORY (*Uncalcined*).

	I. Per cent.	II. Per cent.
Calcium phosphate, including slight amount of calcium fluoride	38.48	46.48
Calcium carbonate	5.63	3.86
Magnesium phosphate	12.01	7.84
Soluble salts	0.70	0.77
Organic matter	43.18	41.05
	100.00	100.00

BONE (*Uncalcined*).

	I. Per cent.	II. Per cent.
Calcium phosphate	61.4	62.4
Calcium carbonate	8.6	7.9
Magnesium phosphate	1.7	1.7
Organic matter	28.3	28.0
	100.0	100.0

401. TYPICAL ANALYSES BY THE AUTHOR OF THE VARIOUS BLACKS.

	I. Ivory Drop Black. Per cent.	II. Lamp-black. Per cent.	III. Lamp-black. Per cent.
Moisture	0.14	2.24	2.18
Oil	0.22	0.35	0.19
Ash	15.23	0.32	0.10
Carbon	84.41	97.09	97.53
	100.00	100.00	100.00

	I. Ivory Black.[1] Per cent.		II. German Ivory Black. Per cent.		III. Ivory Black.[1] Per cent.
Moisture	0.75		2.33		2.59
Oil	0.17		0.22		0.14
Ash	88.98		84.82		84.70
Insoluble 0.88		0.42		0.32	
Calcium phosphate 73.72		77.51		77.82	
Calcium carbonate 14.00		6.51		5.60	
Magnesium phosphate 0.38		0.38		0.96	
Carbon	10.10		12.63		12.57
	100.00		100.00		100.00

[1] Not true ivory blacks.

Analysis of Mixed Paints Tinted with Black and Oxide of Iron Pigments.

402. **Carbon.** One gram of the pigment is dissolved in hydrochloric acid as described under white pigments, and the residue filtered through an ashless filter, that has been dried in the hot-water oven and weighed. After washing the residue with boiling water the filter and contents are dried and weighed, then ignited until all the carbon is burned off, and weighed again. The percentage of carbon is obtained by difference. Where the percentage of color is small, it is often estimated by difference, adding together the determined constituents and subtracting from 100.

403. **Ferric oxide.** If the filtrate from the insoluble

residue is of an appreciable yellow color, it indicates that the tint has been "warmed up" by the addition of an ochre or oxide, in which case the lead is precipitated and estimated as described under analysis of white pigments, the filtrate from the lead sulphide heated until all of the hydrogen sulphide has been expelled and the iron and alumina precipitated with ammonia after having been oxidized by boiling with a few drops of nitric acid, filtered and ignited and weighed in a porcelain crucible, the residue fused with bisulphate of potassium, dissolved in water with the aid of a little hydrochloric acid, heated to boiling, reduced with stannous chloride; mercuric chloride and manganous sulphate solution added and titrated with permanganate in the manner described under analysis of Venetian reds.

404. **Alumina.** The alumina is calculated by difference from the data obtained under 403.

405. **Zinc oxide.** The filtrate from the iron and alumina precipitate and the filtrate from the lead sulphate precipitate, the alcohol having been removed by evaporation, are mixed, made distinctly alkaline with ammonia, and the zinc precipitated with hydrogen sulphide. The liquid containing the zinc sulphide precipitate is heated to boiling, and about 5 grams of solid ammonium chloride added, which renders the precipitate easier to filter. Settle, filter, and wash thoroughly. Pierce filter, wash through into a clean beaker with water, dissolving the residue on filter with dilute hydrochloric acid, and wash with hot water. Dilute, heat to expel hydrogen sulphide, and titrate with ferrocyanide as previously described. If iron is absent in the paint the zinc may be estimated directly as described under analysis of white paints.

406. Calcium and magnesium. Estimate as usual in the filtrate from the zinc sulphide.

407. Residue insoluble in hydrochloric acid. Fuse with sodium carbonate as previously described. Dissolve in water and filter. Iron not previously dissolved will remain on the filter as ferric oxide along with any barium that may be present. This residue after thorough washing is dissolved with the aid of a small quantity of hydrochloric acid, the barium precipitated as usual, and the iron estimated in the filtrate from the barium sulphate. The silica and alumina are estimated as usual.

408. Lead sulphate. Determine the combined sulphuric acid as described under analysis of white paints and calculate to lead sulphate in the absence of calcium sulphate. If calcium carbonate and calcium sulphate are both present the nitric acid-alcohol separation should be used.

409. ANALYSES, BY AUTHOR, OF PAINTS TINTED WITH BLACKS, OCHRE, AND IRON OXIDES.

	I. Light Drab.	II. Drab.
Net weight	6 lbs. 6 oz.	6 lbs. 12 oz.
Capacity of can, qts.	2.06	2.03
Contents, qts.	1.93	1.92
	Per cent.	Per cent.
Pigment by weight	56.6	56.9
Vehicle	43.4	43.1
	100.00	100.00

ANALYSIS OF VEHICLE.

	Per cent.	Per cent.
Linseed oil	92.9	92.0
Turpentine drier	7.0	6.2
Water	0.1	1.8
	100.0	100.0

ANALYSIS OF PIGMENT.

		Per cent.		Per cent.
White lead		26.57		27.73
Lead sulphate		0.78		2.39
Zinc oxide		62.34		57.12
Color		10.31		12.76
Clay and silica	5.56		7.74	
Iron oxide	3.02		3.89	
Carbon and undetermined	1.73		1.13	
		100.00		100.00

410. **Graphite paints.** The term graphite as applied to paints does not necessarily mean that such paints are composed of graphite wholly or even in part. In fact there is no accepted standard of purity for graphite itself. One paint manufacturer may purchase a natural graphite for his line of graphite paints which contains 20 per cent of graphitic carbon, the other 80 per cent being silica and various silicates; others may purchase graphites containing 80 per cent or more of graphitic carbon; and some purchase products which are very nearly pure graphitic carbon, prepared electrically. While it is a far from settled question, perhaps the majority of paint manufacturers and those who buy graphite paints under strict specifications are of the opinion that a graphite paint affords better service value when it contains in part something besides graphitic carbon.

411. **Colored graphite paints.** Having established his graphite paint on the market, the manufacturer soon has requests for colors other than black, and in order to meet the requirements of his trade he finds it necessary to add considerable amounts of tinting pigments, with the natural result that in time many of his formulas contain little or no graphite.

412. The following analyses will give some idea of the pigment combinations to be found on the market:

	I. Natural Graphite. Per cent.	II. Olive Graphite. Per cent.	III. Indian Red Graphite. Per cent.	IV. Seal Brown Graphite. Per cent.
Graphitic carbon	32.14	21.89	...	5.31
Calcium carbonate	42.86	19.16	44.59	26.12
Magnesium silicate and silicate	25.00	...	12.17	33.72
Ochre	...	58.95	...	...
Ferric oxide	...	...	43.24	34.85
	100.00	100.00	100.00	100.00

The pigment portion of one sample analyzed by the author was nothing but Keystone filler; another, carbon black, which while as expensive as the ordinary grades of graphite is nevertheless radically different. Graphite paints which are sold according to specifications for structural iron and steel work are usually high-grade products.

CHAPTER XXII.

ANALYSIS OF BROWN PIGMENTS AND PAINTS.

Vandyke-brown. Composition.

413. Vandyke-browns vary widely in composition according to the method of preparation. Some are obtained from natural deposits of an organic nature, such as peat, decayed vegetable matter, etc.; or by the slight calcining of cork cuttings, bark, and twigs of trees; while some of the more common varieties are prepared by mixing lampblack or other black pigments with sufficient red oxide and ochre to give the desired shade.

414. Analyses of two Vandyke-browns by the author gave the following results:

		I.		II.
Organic matter and moisture		90.95		91.10
Ash		9.05		8.90
Silica	1.90		2.61	
Alumina and ferric oxide	1.43		1.50	
Calcium carbonate	4.98		3.28	
Soluble salts	0.74		1.51	
		100.00		100.00

Analysis of Umbers and Siennas.

415. Hygroscopic moisture. Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

416. Combined water. Transfer above sample to a weighed platinum crucible and heat for 1 hour over an ordinary lamp, or better in a muffle. Loss in weight indicates amount of combined water. Carbonates and

organic matter render the results inaccurate, in which case continue the ignition at bright red heat for several hours, and weigh again. Determine the carbon dioxide in another portion of the sample and estimate the combined water by difference.

417. **Silica and barium sulphate.** One gram of the pigment is intimately mixed with 6 to 8 grams of potassium bisulphate and fused in a large porcelain crucible, the cover of which is small enough to set inside the top of the crucible, at not too high a temperature for one-half hour; finally heating the side of the crucible to finish the conversion of any material adhering to the cover and upper portion of the crucible. The iron, manganese, aluminum, calcium, and magnesium are converted into sulphates, the barytes remains unchanged, and the silica is completely dehydrated.

After cooling, the entire contents of the crucible may be shaken loose and dissolved in sufficient water and a little hydrochloric acid. Filter and make up to 250 c.c.

418. The residue remaining on the filter, which should be white, a red or brownish color indicating incomplete fusion with potassium bisulphate, in which case the sample must be fused again, is ignited, and weighed in a platinum crucible. The residue is tested for barium sulphate by the flame test: if absent, the residue is reported as silica; if present, the residue is treated in the crucible with hydrofluoric acid until a thin paste is formed. The mixture is stirred with a platinum wire and digested at a gentle heat; finally two or three drops of sulphuric acid are added and the temperature gradually raised until no further loss in weight takes place, indicating that the silica has been completely expelled. The residue is weighed as barium sulphate and the loss in weight represents the silica.

419. **Ferric oxide.** An aliquot portion of the solution from 417 is heated nearly to boiling and stannous chloride solution added cautiously until the yellow color has disappeared, and then a slight excess added. All at once with vigorous shaking of the flask 50 c.c. of mercuric chloride solution is added, then 50 c.c. of the manganous sulphate solution. Dilute with cold freshboiled water and titrate with permanganate solution. Calculate iron found to ferric oxide.

420. **Manganese.** Digest 0.5 gram of the sample with 15 c.c. of concentrated hydrochloric acid until all of the iron and manganese has dissolved, then add 5 c.c. of sulphuric acid diluted with 10 c.c. of water, and evaporate on the hot plate until all of the hydrochloric acid is expelled as shown by copious evolution of sulphur trioxide fumes. Cool, dissolve in about 25 c.c. of water, and heat carefully with occasional shaking until all of the anhydrous sulphate of iron has dissolved. Transfer to a 250 c.c. graduated flask and add an excess of zinc oxide emulsion, obtained by mixing C. P. zinc oxide with water. Avoid a large excess, but sufficient to precipitate all the iron, so that on standing the solution begins to settle clear and some zinc oxide can be seen in the bottom of the flask. Cool and make up to the mark.

421. Transfer an aliquot portion to a beaker or flask, and add an excess of a saturated solution of bromine water and about 3 grams of sodium acetate. One c.c. of a saturated solution of bromine water will precipitate about 0.01 gram of manganese. Boil for about 2 minutes. Filter and wash with hot water. The filtrate must be perfectly clear. Place the filter containing the washed precipitate back in the beaker or flask in which the precipitation was made. All traces of bromine must be entirely expelled.

422. Add an excess of standard oxalic acid solution and about 50 c.c. of dilute sulphuric acid (1 : 9) and heat nearly to boiling with gentle agitation until the precipitate is entirely dissolved. Dilute to about 200 c.c. with hot water, and titrate with standard permanganate.

Standard oxalic acid solution. Dissolve 12.6048 grams of chemically pure oxalic acid in freshly boiled water and make to 1000 c.c. in a graduated flask.

One c.c. of this solution = .0055 gram of manganese.

The oxalic acid solution should be standardized against the standard permanganate solution and the correction factor calculated.

Example: Wt. of sample taken = 0.5 gram.
Volume of solution = 250 c.c.
Aliquot portion used = 100 c.c. = 0.2 gram.
1 c.c. of permanganate sol. = 0.499 c.c. of oxalic acid.
1 c.c. of oxalic acid sol. = 0.0055 gram of manganese.

Permanganate solution used in titrating excess of oxalic acid solution = 13.2 c.c.

13.2 c.c. = 6.59 c.c. of oxalic acid.

Oxalic acid solution used,	10.00 c.c.
Excess,	6.59 c.c.
Consumed,	3.41 c.c.

$3.41 \times .0055 = .018755$ g. Mn.

$Mn : MnO_2 : .018755 : x.$

$x = .02967$ g. MnO_2.

$.02967 \div 0.2 = 14.84$ per cent MnO_2.

423. **Alumina.** Fifty c.c. of the 250 c.c. solution prepared in 417 is treated with about 20 grams of solid

ammonium chloride, made just alkaline with ammonia, heated, allowed to settle, decanted, filtered, and washed. The precipitate is dissolved on the filter with hydrochloric acid and, after washing with small portions of boiling water, the iron and aluminum is reprecipitated, solid ammonium chloride being added as before. The precipitate is washed by decantation, filtered, and the filtrate collected in the beaker containing the first filtrate. This treatment frees the iron and aluminum from any manganese and the precipitate may be dried, ignited, and weighed in the usual manner, the alumina being obtained by difference. It is often advisable to make another reprecipitation of the iron and alumina, using but a small amount of ammonium chloride.

424. **Calcium and magnesium.** The combined filtrates from the iron and alumina are treated with colorless ammonium sulphide in such a manner as to form the green sulphide of manganese, which is very much easier to filter than the pink sulphide.

The colorless ammonium sulphide may be prepared as follows: Saturate one-half of a solution of 100 c.c. of water and 50 c.c. of ammonia (sp. gr. 0.90) with hydrogen sulphide, and then add the other half of the solution.

For the precipitation of the manganese, 25 c.c. of the ammonium sulphide solution and 10 c.c. of ammonium chloride solution containing 3 grams of the dry salt are placed in an Erlenmeyer flask, the solution diluted to about 100 c.c. and heated. As soon as it comes to a boil, the combined filtrate from the iron and alumina is added and the beaker rinsed with a little water. The flask is shaken vigorously and the solution kept nearly at the boiling point. After alternate shaking

and heating, the pink sulphide of manganese turns green and settles readily, leaving a clear supernatent liquid. If the ammonium sulphide is of the proper strength and a sufficient amount be used, there should be no difficulty in obtaining the green sulphide in proper condition for filtering.

After filtering off the manganese, the filtrate is evaporated to a syrupy consistency and 20 c.c. of nitric acid (sp. gr. 1.2) added in small portions, evaporating each time. Sufficient hydrochloric acid is added and heat applied, until the brown fumes cease to be given off. This treatment, which removes the excess of ammonium salts, is not necessary if magnesium is known to be absent.

The solution, after the removal of the nitric acid, is diluted with water, made alkaline with ammonia, and the calcium and magnesium separated and estimated in the usual manner, both being calculated to the oxides. The calcium may have been present as carbonate or sulphate or both. Hence an estimation of the combined sulphuric acid present in the original sample is necessary. For this purpose 1 gram is dissolved in 30 c.c. of strong hydrochloric acid boiled 10 minutes, diluted with 50 c.c. of water heated to boiling, filtered, and washed with hot water. Neutralize the filtrate with ammonia, then make just distinctly acid with hydrochloric acid, boil, add 10 c.c. of barium chloride solution, continue boiling for 10 minutes, filter, wash, ignite, and weigh as barium sulphate. Calculate combined sulphuric acid by multiplying weight of precipitate by 0.343.

Calculate the combined sulphuric acid found to calcium sulphate and the remaining calcium to oxide.

425. ANALYSES OF UMBERS AND SIENNAS BY THE AUTHOR.

	I. Raw Sienna.	II. Burnt Sienna.
Moisture	0.42	0.44
Loss on ignition	12.28	12.67
Silica	36.85	19.55
Ferric oxide	45.18	62.75
Alumina	3.00	1.66
Calcium oxide	1.09	2.52
Magnesium oxide	0.85	0.00
Sulphur trioxide	0.15	0.20
Manganese dioxide	0.13	0.17
Undetermined	0.05	0.04
	100.00	100.00

	III. Raw Umber.	IV. Burnt Umber.
Moisture	1.78	2.01
Loss on ignition	13.64	3.94
Silica	20.60	24.21
Ferric oxide	42.60	51.04
Alumina	2.90	6.80
Calcium oxide	3.68	1.95
Magnesium oxide	2.16	...
Sulphur trioxide	0.36	0.22
Manganese dioxide	11.95	9.79
Undetermined	0.33	0.04
	100.00	100.00

Analysis of Mixed Paints Containing Umbers, Siennas, and Ochres.

426. Determine the manganese in a separate sample as determined under the analysis of umbers. Determine the lead as in white paints, using the filtrate from the lead sulphide for the estimating of the iron, which must be oxidized by boiling with a little nitric acid before precipitating. Determine aluminum, zinc, calcium, and magnesium as described under analysis of umbers and siennas. The zinc being precipitated as the sulphide after the removal of the iron and aluminum is

contaminated with manganese sulphide. Dissolve the mixed sulphides in dilute hydrochloric acid, boil until the odor of hydrogen sulphide is expelled. Cool. Add excess of sodium hydroxide and filter off the precipitated manganese hydroxide, washing thoroughly. The filtrate containing the zinc in solution as sodium zincate is acidified with hydrochloric acid, heated to about 80° C., and titrated with potassium ferrocyanide in the usual manner.

Any barytes, silica, and insoluble silicates are separated and estimated as usual.

CHAPTER XXIII.

ANALYSIS OF BLUE PIGMENTS AND PAINTS.

Analysis of Prussian Blues, Chinese Blues, etc.

427. **Hygroscopic moisture.** Heat 2 grams to 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

428. **Water of combination.** The water of combination (so called) cannot with advantage be determined directly, but can be approximated by subtracting the total per cent of constituents determined — hygroscopic moisture, cyanogen, iron, aluminum, alkali metal, alkaline sulphate, and inert base, if any — from 100 per cent.

429. **Iron.** Ignite 1 gram at a temperature sufficient to decompose the last trace of the blue, but not so high as to render the oxide of iron difficult of solution. Dissolve in 25 c.c. of hydrochloric acid and 25 c.c. of water with aid of heat. Filter, making up filtrate to 250 c.c. Titrate 50 c.c. with potassium permanganate, after adding stannous chloride, mercuric chloride, and manganous sulphate solution in the usual manner. Calculate to metallic iron.

430. **Aluminum.** Precipitate the iron and aluminum from 50 c.c. of the iron solution. Filter, ignite, and weigh, estimating the alumina by difference. It probably exists in the Prussian blue as aluminum ferrocyanide. Calculate to metallic aluminum.

431. **Calcium.** Calcium compounds are very rarely found in Prussian blues. If the Prussian blue is precipitated on barytes, the latter is liable to contain a small amount of calcium carbonate as an impurity. Treat the filtrate from 430 with ammonium oxalate. Settle, filter, ignite, and weigh as calcium oxide. Calculate to calcium carbonate.

432. **Alkali metal and alkaline salts.** The filtrate from 431 is evaporated to dryness in a weighed evaporating dish, the ammonium salts completely volatilized, the alkaline salts weighed, and the chlorine therein determined by titration with standard silver nitrate solution. The alkali metal is, almost without exception, entirely sodium or potassium and not a mixture of the two, and may be identified by the flame test, using a small fragment of the weighed alkaline salt. The sulphuric acid is estimated, in 50 c.c. of the solution, in the usual manner. The amount obtained is calculated to sodium sulphate or potassium sulphate, as the case may be. The potassium or sodium chemically combined with the Prussian blue is calculated from the amount of chlorine found and reported as metallic sodium or potassium.

433. **Cyanogen.** Estimate the nitrogen in 1 gram of the sample by the Kjeldahl-Gunning method. Multiply the nitrogen obtained by 1.86 to convert it into cyanogen.

434. **Barytes, silica, clay, etc.** The insoluble portion remaining on the filter paper in 429 is ignited and weighed. Fuse with sodium carbonate and estimate the barytes, silica, alumina, etc., as described under analysis of white paints.

435. **Calculations.** The amount of Prussian blue may be calculated approximately by multiplying the iron content by 3.03 or the nitrogen content by 4.4. These

factors are not exact, as Prussian blues have varying compositions.

A Prussian blue to be considered pure should contain at least 20 per cent of nitrogen and 30 per cent of iron calculated on the dry matter and after burning should be entirely soluble in hydrochloric acid. A dry blue should contain less than 7 per cent moisture, and the sulphuric acid in the Kjeldahl nitrogen determination should not be blackened, which would indicate organic adulteration.

436. ANALYSES OF "PURE" PRUSSIAN BLUES.[1]

	I.	II.	III.	IV.
Moisture (lost at 100° C.)	5.61	3.54	5.36	5.45
Water of combination, etc.	15.46	18.18	6.22	13.07
Cyanogen	37.72	41.10	42.97	37.90
Iron	29.48	32.16	34.27	30.32
Aluminum	1.82	.52	...	3.17
Alkali metal (Na)	7.60	(K) 4.50	(K) 7.72	(K) 2.25
Alkaline sulphate	2.31	...	3.46	7.84
	100.00	100.00	100.00	100.00

	V.	VI.	VII.	VIII.
Moisture (lost at 100° C.)	74.53	5.32	5.56	5.61
Water of combination, etc.	3.08	7.86	14.60	16.93
Cyanogen	10.64	39.91	40.19	40.86
Iron	7.97	30.94	31.94	31.25
Aluminum	.72	1.00	1.43	1.52
Alkali metal (Na)	(K) 1.06	(K) 11.31	Na 2.52	.76
Alkaline sulphate	2.00	3.66	3.76	Na 3.07
	100.00	100.00	100.00	100.00

[1] Parry and Coste, The Analyst, Vol. XXI., page 227.

437. ANALYSES OF CHINESE BLUES BY AUTHOR.

	I.	II.	III.
Moisture (lost at 100° C.)	2.49	3.45	2.04
Water of combination, etc.	12.69	18.12	8.75
Cyanogen	45.78	36.51	46.09
Iron	35.87	32.34	35.86
Aluminum	...	...	...
Alkali metal	Na 1.57	(K) 4.89	Na 3.80
Alkaline sulphate	1.50	3.61	3.35
Silica	0.10	1.08	0.11
	100.00	100.00	100.00

Analysis of Mixed Paints Containing Prussian Blue, Chinese Blue, etc.

438. Weigh 1 gram into a 250 c.c. beaker, add 30 c.c. of concentrated hydrochloric acid, boil 5 minutes, add 50 c.c. of hot water, boil 10 minutes, filter. Wash thoroughly with boiling water. Ignite, filter, and precipitate gently, so as to destroy the blue color but not at a sufficiently high temperature to render the iron oxide difficultly soluble in acid. Cool, digest in moderately concentrated hydrochloric acid until the iron is all dissolved. Dilute, filter, adding this filtrate to the first filtrate. The insoluble residue is ignited, weighed, and fused with sodium carbonate, the barium, silica, and alumina separated as described under analysis of white paints. The lead, iron, soluble aluminum, zinc, and any calcium and magnesium compounds separated and estimated as described under analysis of mixed paints containing blacks and oxide of iron pigments.

439. If the paint in question is free from other iron pigments, the percentage of Prussian blue may be calculated by multiplying the iron content by 3.03. If other iron pigments are present the nitrogen content must be determined; this multiplied by 4.4 will give the approximate amount of Prussian blue present.

Analysis of Ultramarine.

440. **Properties.** Ultramarine is a compound of silica containing alumina, soda, sulphur, and combined sulphuric acid. It has been often stated that ultramarine cannot be mixed with white lead, because of the sulphur content of the ultramarine, but the author has ascertained that a great many paint manufacturers

use it in tinting mixed paints where the percentage of white lead does not exceed that of the zinc, without any harmful results following. Ultramarines that are to be used in the manufacture of paper should be tested for their power of resisting the action of alum, by boiling 5 grams in a 5 per cent alum solution. As found on the market, ultramarines vary much in tint, brilliance, and coloring power.

441. **Moisture.** Heat 2 grams at 1.05° C. for 3 hours, cool, and weigh.

442. **Silica.** Digest 1 gram in a casserole provided with a beaker cover, with 30 c.c. of concentrated hydrochloric acid. Evaporate to complete dryness, cool, add 2 c.c. of concentrated hydrochloric acid, evaporate to dryness, and heat gently for 15 minutes. Take up in 100 c.c. of hot water, add 10 c.c. of hydrochloric acid. Filter, ignite, and weigh as silica.

443. **Alumina.** The filtrate from the silica is made just sufficiently alkaline with ammonia to precipitate the aluminum. Heat gently, filter, ignite, and weigh as alumina.

444. **Sodium oxide.** The filtrate from the alumina is neutralized with sulphuric acid in a porcelain evaporating dish, evaporated to dryness, the residue treated with a little sulphuric acid, evaporated to dryness again, treated with water, evaporated to dryness, and ignited at low red heat, cooled, and weighed.

Wt. sodium sulphate $\times$ 0.4366 = wt. of sodium oxide.

445. **Total sulphur.** Fuse 1 gram in a large crucible with a mixture of potassium nitrate and potassium chlorate for about half an hour. Dissolve the fused mass in dilute hydrochloric acid and boil the solution with strong nitric acid for half an hour, filter off the

silica and precipitate the sulphuric acid with barium chloride in the usual manner. Filter, ignite, and weigh as barium sulphate.

From the weight of barium sulphate thus obtained deduct the weight found in 446; the difference is the amount due to sulphur present in the blue as sulphide.

Wt. barium sulphate $\times$ 0.1373 = wt. sulphur.

446. Combined sulphuric acid. Dissolve 1 gram in dilute hydrochloric acid. Filter off the silica, make filtrate alkaline with ammonia and then just distinctly acid with hydrochloric acid, and treat with barium chloride in the usual manner. The precipitated barium sulphate is filtered, ignited, and weighed as usual.

Wt. barium sulphate $\times$ 0.3434 = wt. of sulphur trioxide.

447. ANALYSES OF ULTRAMARINES BY THE AUTHOR.

	Ultramarine Blue. I.	Ultramarine Blue. II.	Ultramarine Blue. III.
Silica	39.26	39.45	41.92
Alumina	25.60	25.81	26.21
Sulphur	11.69	12.02	10.82
Sulphur trioxide	3.10	2.33	1.93
Sodium oxide	19.87	19.73	18.40
Water	0.48	0.66	0.72
	100.00	100.00	100.00

448. ANALYSES OF ULTRAMARINES BY HURST.

	Sulphate.	Soap Makers.	Calico Printers.	Paper Makers.
Silica	49.69	40.65	40.89	45.42
Alumina	23.00	25.05	24.11	21.15
Sulphur	9.23	12.95	13.74	11.62
Sulphur trioxide	2.46	4.81	3.05	5.58
Soda	12.49	14.26	15.61	9.91
Water	3.13	2.28	2.60	6.32
	100.00	100.00	100.00	100.00

Analysis of Cobalt Blue.

449. This pigment, which is essentially a compound of the oxides of alumina and cobalt, has largely gone out of use, but that it still finds a limited application is evidenced by the fact that the author receives occasionally samples for analysis. Certain shades of ultramarine blue are often sold under the name of cobalt blue.

450. **Moisture.** Determine as usual.

451. **Alumina.** Fuse 1 gram with potassium bisulphate as described under analysis of Indian reds and Venetian reds. Dissolve in water and hydrochloric acid, filter, and make up to 250 c.c. in a graduated flask. Any residue remaining on the filter paper is ignited and weighed as silica, unless barium sulphate is present, which would be shown by the flame test.

An aliquot portion of the solution is treated with an excess of ammonium chloride, and then made just distinctly alkaline with ammonia. Filter, dissolve on the filter with hydrochloric acid, and reprecipitate. Filter again, combining the two filtrates. Wash thoroughly, ignite, and weigh as alumina.

452. **Calcium and magnesium.** The combined filtrates from the alumina are saturated with hydrogen sulphide, filtered, and any calcium and magnesium estimated in the filtrate in the usual manner.

453. **Cobalt oxides.** The oxides of cobalt present are best estimated by difference, by subtracting the determined constituents from 100. It is stated by Hurst that phosphoric acid is occasionally used in the manufacture of cobalt blues, in which case it should be removed before estimating the aluminum, calcium, and magnesium. The several samples examined by the author were found to be free from phosphoric acid.

CHAPTER XXIV.

ANALYSIS OF YELLOW, ORANGE, AND RED CHROME LEADS; ANALYSIS OF VERMILIONS.

454. Composition. The lemon yellow chromes usually contain sulphate of lead, sometimes carbonate of lead. The red chromes, known by the various names of scarlet chrome, chrome red, Chinese red, American vermilion, and vermilion substitute, may be considered as basic chromates of lead. Often these basic chromes are brightened up by having precipitated on them an organic color; this may be tested for by treating a portion of the pigment with alcohol, which will dissolve the organic color, giving a strongly colored solution. See analysis of vermilions.

455. Hygroscopic moisture. Heat 2 grams at 105° C. for 3 hours. Loss in weight represents hygroscopic moisture.

456. Barytes, silica, and clay. One gram of the pigment is boiled for 5 minutes with 30 c.c. of concentrated hydrochloric acid in a covered beaker. While boiling add half a dozen drops of alcohol one at a time. Fifty c.c. of water is added and the boiling continued for 10 or 15 minutes. Filter, wash thoroughly with boiling water, ignite, and weigh. The insoluble residue is fused with sodium carbonate, and the barium, silica, and alumina separated as described under analysis of white paints.

457. Lead. The filtrate from the insoluble residue is neutralized with dilute ammonia until the further addi-

tion of another drop would cause the formation of a permanent precipitate, diluted to about 250 c.c. to 300 c.c., and hydrogen sulphide passed in for 10 minutes.

Solutions containing large amounts of chromium, if neutralized with ammonia until a permanent precipitate appears, seem to require an excess of hydrochloric acid for their resolution, sufficient to prevent the satisfactory precipitation of the lead with the hydrogen sulphide.

Allow the precipitate to settle thoroughly, as it renders the filtering much easier, filter, wash with hydrogen sulphide water. Boil, filter, and precipitate with dilute nitric acid, until all of the lead has dissolved, filter with aid of suction, washing thoroughly with hot water. Add 5 c.c. of concentrated sulphuric acid, diluted with an equal volume of water, to the filtrate. Evaporate on hot plate until the white fumes of sulphur trioxide appear. Cool, dilute with water, add an equal volume of alcohol, filter, washing with dilute alcohol, ignite gently, and weigh as lead sulphate. Save filtrate.

458. **Chromium.** The alcoholic filtrate from the lead sulphate is evaporated nearly to dryness to expel alcohol, and the filtrate from the lead sulphide heated until the hydrogen sulphide is expelled. The two filtrates are mixed, diluted if necessary, and made just perceptibly alkaline with ammonia; boil, settle, filter, wash thoroughly, ignite, and weigh as chromic oxide.

Wt. chromic oxide $\times$ 1.3137 = wt. chromic anhydride.

Occasionally these pigments contain a small quantity of iron, which should be tested for qualitatively in a separate portion of the pigment. If found to be present, the precipitate of ferric and chromium hydroxides is dissolved on the filter with hydrochloric acid,

the filter washed thoroughly with hot water, and the iron and chromium in the filtrate reprecipitated with ammonia and treated with sodium peroxide to dissolve the chromium as described under the analysis of chrome greens.

459. **Calcium.** The filtrate from the chromium is treated with ammonium oxalate, allowed to stand in a warm place for an hour or so, filtered, washed thoroughly, strongly ignited, and weighed as calcium oxide.

460. **Magnesium.** The magnesium is estimated in the filtrate from the calcium in the usual manner.

461. **Combined sulphuric acid.** The combined sulphuric acid may be estimated by either of the two methods given in the chapter devoted to the analysis of white paints. In fact, the latter method may be used for the rapid analysis of a chrome lead, the insoluble lead carbonate being filtered off, the chromium precipitated as the hydroxide in the usual manner, and the combined sulphuric acid estimated in the filtrate from the chromium.

Wt. barium sulphate $\times$ 0.3433 = combined sulphuric acid.

462. **Calculations.** If calcium is absent, or present as carbonate, the combined sulphuric acid is calculated to lead sulphate, the chromic anhydride to lead chromate, and excess of lead to lead oxide. If calcium sulphate and carbonate of lead are present, the carbon dioxide must be determined and the amount of calcium present as sulphate estimated by Thompson's method as described under analysis of white paints.

Wt. comb. sulphuric acid $\times$ 3.788 = wt. lead sulphate.

Wt. chromic anhydride $\times$ 3.230 = wt. lead chromate.

Wt. lead chromate $\times$ 0.6406 = wt. lead.

Wt. lead $\times$ 1.0773 = wt. lead oxide.

The specifications for chrome leads issued by the U. S. Treasury Department, 1907, state that a color containing lead sulphate is to be preferred to one containing white lead.

463. ANALYSES OF CHROME LEADS BY AUTHOR.

	Light Chrome Yellow.	Deep Orange Chrome Yellow.
Moisture	0.04	0.03
Lead chromate	68.65	40.56
Lead oxide	...	47.24
Lead sulphate	31.21	5.49
Silica	...	0.74
Alumina	...	0.44
Organic color	...	4.87
Undetermined	0.10	0.63
	100.00	100.00

Analysis of Mixed Paints Containing Chrome Yellows and Ochres.

464. **Barytes, silica, and clay** are estimated as described under analysis of chrome leads.

465. **Lead,** both as sulphate and carbonate, is estimated as described under chrome leads, the filtrate from the lead sulphate being saved as before.

466. **Iron.** The filtrate from the lead sulphide is heated until all of the hydrogen sulphide has been expelled and added to the filtrate from the lead sulphate from which the alcohol has been expelled by boiling. A few drops of nitric acid are added and the solution boiled for a minute or two, then made just distinctly alkaline with ammonia, boiled, settled, and filtered.

Dissolve on the filter with hot dilute hydrochloric acid, wash with hot water. *Cool.* Reprecipitate with

ammonia, avoiding excess, without waiting for the precipitate to settle, carefully add a sufficient quantity of sodium peroxide (1 gram is usually sufficient), keeping the beaker covered meanwhile. Digest until all of the chromium and aluminum have passed into solution, adding more peroxide if necessary. The iron remains undissolved, while the chromium and aluminum go into solution; filter, wash thoroughly, ignite strongly, and weigh as ferric oxide, or dissolve in dilute hydrochloric acid and titrate. The treatment with peroxide is preferably performed in a porcelain evaporating dish.

467. **Chromium.** The filtrate from the iron is made up to 250 c.c. in a graduated flask. An aliquot portion is rendered acid with acetic acid and a slight excess of lead nitrate solution added, allowed to remain on the hot plate until thoroughly settled, filtered onto a weighed Gooch crucible, washed, dried, and weighed as lead chromate.

468. **Aluminum.** An aliquot portion of the 250 c.c. solution is made just acid with hydrochloric acid, and then just distinctly alkaline with ammonia, allowed to settle, filtered onto a Gooch crucible, ignited, and weighed as alumina.

469. **Zinc.** The filtrate from the chromium, iron and aluminum hydroxides, under iron is mixed with the filtrate from the lead sulphate from which the alcohol has been expelled, and the mixed solution saturated thoroughly with hydrogen sulphide, boiled with the addition of solid ammonium chloride to render the precipitate less slimy, and filtered. The zinc sulphide dissolved with hydrochloric acid, boiled to expel hydrogen sulphide, and titrated with standard ferrocyanide of potassium as described under analysis of white paints.

470. Calcium, magnesium, and combined sulphuric acid are estimated as described under analysis of chrome leads and the calculations made as there described.

Analysis of Vermilion.

471. Properties. Vermilion is a bluish scarlet powder, having a specific gravity of 8.2. It is insoluble in any single acid such as hydrochloric or nitric acid and in the alkalies. Heated in contact with the air, it burns with a pale blue lambent flame. Pure vermilion will burn away entirely or at least leave but a small fraction of 1 per cent of ash. This is a reliable test for it, as other adulterants would be left behind on heating.

The most common adulterants of vermilion are red lead, oxide of iron, lead chromes, vermilionette lakes, para reds, and alizarine reds.

472. Detection of vermilionettes, para and alizarine reds. (*a*). Boil a little of the dry color with water, settle, and filter. Vermilionettes give a deep red solution, para reds a pale brownish or orange, and the alizarine reds a colorless solution.

(*b*). Boil a little of the dry color with a mixture of methyl and ethyl alcohol, filter, heat, and settle. Vermilionettes give a bright red solution, usually having a yellow "bloom," para reds an orange-red solution, alizarine reds a practically colorless solution.

(*c*). Boil another portion of the dry pigment with some freshly distilled aniline, settle, and filter. Vermilionettes give a purple-red, alizarine lakes a pale brown, and the para reds an intense orange-red solution.

(*d*). Boil some of the dry color with a solution of caustic soda. Vermilionettes give a red solution with

a green "bloom," para reds a bluish red solution, while alizarine reds yield a characteristic deep violet solution.

473. **Barytes, silica, and clay.** Dissolve 1 gram in 30 c.c. of concentrated hydrochloric acid, 50 c.c. of water with the aid of 1 to 2 grams of potassium chlorate added in small portions and warming. Evaporate to dryness on water bath. Take up in 50 c.c. of water acidulated with hydrochloric acid, heat to boiling to dissolve any lead chloride, filter, wash with boiling water, ignite, and weigh any insoluble residue. Fuse with sodium carbonate and estimate the barium sulphate, silica, and alumina as described under analysis of white paints.

474. **Lead.** If lead is present, calcium compounds being absent, the filtrate is treated with sulphuric acid, evaporated carefully to expel excess of hydrochloric acid, diluted with water and alcohol, the lead sulphate filtered off on a Gooch crucible in the usual manner.

475. **Mercuric sulphide (vermilion).** The filtrate from the insoluble residue, if lead is absent, or the filtrate from the lead sulphate, is heated with a little sulphurous acid to reduce any iron present to the ferrous condition, made neutral with ammonia, and then *just* acid to litmus with hydrochloric acid.

The solution is diluted to about 350 c.c. and hydrogen sulphide passed in for 10 minutes. The mercuric sulphide is filtered off on a weighed Gooch crucible, washed with hydrogen sulphide water, the crucible removed to another holder and washed with alcohol and carbon bisulphide to remove sulphur, dried in steam oven, and weighed.

476. **Estimation of lead and mercury, calcium compounds present.** The filtrate from the insoluble residue

from 473 is precipitated with hydrogen sulphide as described under 475, collected on a weighed filter, and dried at 100° C., weighed, and mixed uniformly.

An aliquot part is introduced into the bulb of Fig. 10, a slow stream of washed chlorine gas passed through it,

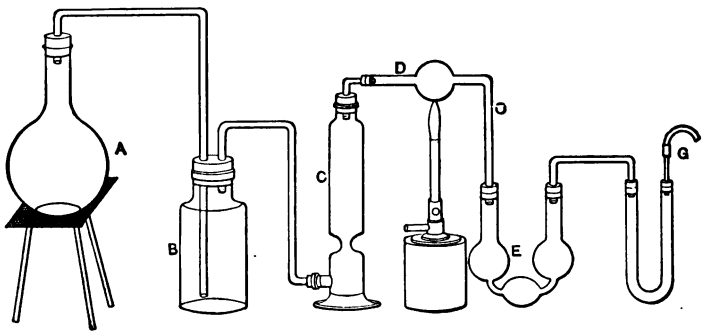

FIG. 10.

and a gentle heat applied to the bulb, increasing this gradually to faint redness. The escaping chlorine is conducted into a flue. First, sulphur chloride distills over, which decomposes with the water in *E* and *F*. The mercuric chloride formed volatilizes, condensing partly in *E*, partly in *O*. Cut off that part of the tube, rinse the mercuric chloride into *E*, and mix the contents of the latter with the water in *F*. Mix the solution with excess of ammonia and warm gently until no more nitrogen is evolved, acidify with hydrochloric acid, filter, and determine the mercury in the filtrate as under 475.

477. **Ferric oxide.** The filtrate from the sulphides is heated until all of the hydrogen sulphide has been expelled and the iron chromium and alumina precipitated with ammonia, filtered and separated as described under analysis of chrome greens.

478. Zinc oxide. The filtrate from the iron and alumina precipitate is made distinctly alkaline with ammonia and the zinc precipitated with hydrogen sulphide. The liquid containing the zinc sulphide precipitate is heated to boiling, and about 5 grams of solid ammonium chloride added, which renders the precipitate easier to filter. Settle, filter, wash thoroughly. Pierce filter, wash through into a clean beaker with water, dissolving the residue on filter with dilute hydrochloric acid, and washing with hot water. Dilute, heat to expel hydrogen sulphide, and titrate with ferrocyanide as previously described. If iron is absent in the paint, the zinc may be estimated directly as described under analysis of white pigments.

479. Calcium and magnesium. Estimated as usual in the filtrate from the zinc sulphide.

480. Calculations. If chromium is present it is calculated to basic lead chromate, and any excess of lead above that required to form the chromate is calculated to red lead.

481. ANALYSES OF VERMILIONS BY THE AUTHOR.

	I. English Vermilion. Deep.	II. English Vermilion. Pale.	III. Vermilion.
Sulphide of mercury	99.53	99.61	99.61
Ash	0.47	0.39	0.39
	100.00	100.00	100.00

	I. Vermilion.	II. Radium Vermilion.
Moisture	0.16	0.06
Red lead	80.08	97.99
Barytes	16.83	...
Alumina	0.77	...
Organic color	2.16	1.95
	100.00	100.00

	I. Light Vermilion.	II. Deep Vermilion.
Moisture	1.33	0.15
Lead chromate	50.16	53.60
Lead oxide	41.20	40.88
Lead sulphate	6.15	4.97
Ferric oxide	0.37	0.33
Soluble salts	0.33	trace
Undetermined	0.46	0.07
	100.00	100.00

482. Antimony vermilion and orange. These two pigments have the same composition, corresponding to the formula of antimony trisulphide. They are insoluble in dilute acids, but soluble in strong hydrochloric acid. It is seldom necessary to make a complete analysis of these pigments. Adulteration will be indicated by the pigment not being completely soluble in strong hydrochloric, though a trace of sulphur may remain undissolved, floating on top of the acid.

CHAPTER XXV.

ANALYSIS OF RED LEAD, ORANGE MINERAL, AND LITHARGE.

483. Red lead. This pigment, corresponding to the formula Pb_3O_4, is prepared by three different processes:

1. The *drossing* process, in which a puddle of molten lead is slowly drossed in a reverberatory furnace by constant rabbling, and the dross or massicot thus obtained is water ground and floated to free from metal particles and calcined for about 48 hours at a definite temperature in another reverberatory furnace. The product is usually bolted through a silk bolting cloth.

2. The *nitrate* process, in which metallic lead and nitrate of soda are fused together, yielding an oxide of lead (PbO) and nitrite of soda ($NaNO_2$). This oxide, after having been thoroughly leached to remove the nitrite, is calcined and finished as above described. The nitrite of soda obtained by this process has a large use in the manufacture of para reds. Red lead manufactured by this process will usually contain a small amount of caustic soda and nitrite of soda.

3. The *basic oxide* process, in which molten lead is very finely subdivided by superheated steam, converted into a basic oxide by agitation with air and water, dried, ground, and calcined for about 15 hours, which is sufficient to develop the full color. This process represents the latest and most advanced stage of oxide manufacture, yielding for many purposes a much superior product.

484. A thorough physical examination of red lead is of fully as much importance as a chemical analysis.

485. **Microscopical examination.** Under the microscope the red lead should show freedom from metallic particles, vitrified red-lead particles, and foreign matter such as coal dust, furnace grit, etc.

486. **Fineness.** Less than one-tenth of 1 per cent should be retained on a screen composed of number 20 or 21 silk bolting cloth.

487. **Color.** The color of red lead, as of the chrome leads, depends on the size of the particles: the larger the particles the deeper the tone, and the smaller the particles the paler the color but with a marked increase of fire and brilliancy. For the manufacture of reduced red leads and of vermilions the deep tones are the most desirable, as they require less dye.

488. **Bulking figure.** Hitherto, the great objection to the use of red lead for painting structural iron and steel work has been its excessive tendency to settle in the paint pot, preventing uniform application and a manifest sagging and streaking. This is due both to the density and the comparative large size of the red-lead particles as compared with other well-known pigments. The first two processes above described produce a red lead having these characteristics, while the third affords a very soft, bulky, amorphous red lead, the particles of which are of a very uniform fineness. In fact, red lead made by this process much resembles orange mineral, having considerable fire and brilliancy, and does not readily settle in the paint pot or sag on vertical surfaces.

Other factors being equal, the bulkiest or least dense red lead is the most desirable for painting purposes. Red leads made by the first two processes give a bulking

figure of from 23 grams to 32 grams per cubic inch by the Scott volumeter.

489. If a liberal percentage of carbonate tailings from the Dutch process of white-lead manufacture has been used, the bulking figure may go as low as 20 grams. The third process yields a red lead having a bulking figure of 15 grams to 18 grams. The writer firmly believes that users of red lead would secure a much increased service value if they would specify a red lead having a bulking figure of 20 grams or under.

490. **Painting test.** When mixed with pure linseed oil, pure turpentine and Japan drier as per the U. S. Navy Department formula (1909), viz:

Red lead, dry	17 pounds
Raw linseed oil	4½ pints
Spirits of turpentine	1 gill
Japan drier	1 gill

and applied to a smooth, vertical iron surface, it must dry solidly without running, streaking, or sagging. It should be noted that while this formula affords a good test for red leads of a moderate bulking figure, it affords a mix entirely too thick with a red lead having a bulking figure of 15 grams to 18 grams.

491. **Free Litharge.** The free litharge content of red lead is a rather variable quantity; it may go as high as 25 per cent or as low as 1 per cent, the average being perhaps between 6 and 12 per cent. No absolutely satisfactory method has yet been devised for its determination. The acetate method is probably as satisfactory as any.

492. Weigh 10 grams of the sample into a 150 c.c. beaker provided with a cover glass, add 25 c.c. of a neutral normal solution of acetate of lead and 50 c.c. of *freshly boiled* distilled water. Boil gently for ex-

actly 5 minutes. Decant onto a Gooch crucible, wash by decantation with boiling water twice, collect residue on crucible, and wash thoroughly with boiling water, then with a few drops of alcohol dry in steam oven, cool, and weigh. The weight of the residue subtracted from 10 indicates the amount of free litharge present. The government specifications require at least 94 per cent true red-lead content, which insures a litharge content of 6 per cent or less.

493. **Peroxide content.** Numerous methods have been devised for determining the peroxide content of red lead. Mannhardt's method is perhaps the most accurate.

Weigh out 1 gram of the pigment. Triturate this with 1.176 grams of ammonium ferrous sulphate crystals. 0.1176 gram of the salt corresponds to 1 c.c. of 3 N-10 (oxidizing) solution and to .03585 PbO_2. The trituration is carried out carefully. The mixture is then brushed into a small beaker and about 10 grams commercial ammonium chloride added. This is moistened and the pigment stirred in and 20 c.c. of water and 20 c.c. of hydrochloric acid added. The mixture is warmed on the steam plate and then titrated for excess of ferrous iron with a 3 N-10 oxidizing solution of bichromate (29.5 grams to 2 liters), using a pale yellow solution of potassium ferrocyanide as external indicator. The ferrous solution must be very strongly acid when nearing the endpoint, in order to obtain a very definite endpoint.

The weight of ferrous ammonium sulphate used in the determination of the peroxide should be about 5 per cent in excess of the theoretical consumption.

The range of consumption of ferrous salt will vary between 7 c.c. and 9.6 c.c. of the bichromate solution.

494. **Orange mineral.** This product may be considered as a debased form of red lead, inasmuch as it is not so stable toward light as red lead. It is usually prepared by calcining white-lead residues or tailings. Its specific gravity is much lower than that of red lead. It may be differentiated from red lead by microscopical examination. Under a magnification of 400 to 500 diameters the particles of red lead much resemble small crystals of bichromate, being distinctly transparent, while orange-mineral particles are much smaller and quite opaque.

495. The same physical and chemical determinations that apply to red lead apply to orange mineral. The litharge content of orange mineral is usually very low, and for this reason it is often ground in linseed oil and put on the market in paste form, whereas the higher litharge content of red lead would cause "livering" and hardening in the package except in occasional instances when a very carefully selected red lead is used.

496. **Litharge.** The different brands of litharge found on the market will vary greatly in color and other physical characteristics, which are determined by the preference of the buyer. The three leading impurities which are of interest to the paint chemist are metallic lead, sulphates, and red lead, all three usually being classed together as "insoluble matter." The metallic lead and red lead are particularly objectionable to the color maker, as they affect the purity of the tint of his colors, they not being soluble in acetic acid. The insoluble matter may be determined by boiling 5 grams of the sample with dilute acetic acid, filtering onto a Gooch crucible, washing thoroughly with hot water, drying, and weighing. The insoluble matter should not exceed 0.6 per cent.

497. Carbon dioxide. Freshly prepared litharge is free from combined carbon dioxide, as the temperature at which it is furnaced is more than sufficient to decompose any carbonate of lead that might be present. On exposure to air, however, litharge absorbs carbon dioxide in notable quantities. This is especially true of samples of litharge sent by mail in paper envelopes or of samples allowed to remain in the laboratory. The determination of carbon dioxide can be made in the usual manner, although the shipment of goods in bulk will usually show practically entire absence of carbon dioxide.

498. Sulphates. The commercial grades of litharge will contain a small fraction of 1 per cent of sulphate of lead, due to the sulphur gases from the coal used in the furnacing. The sulphate content can be determined as stated in the chapter devoted to the analysis of white lead. The small quantity usually found is not objectionable for dry-color manufacture, as it undergoes conversion with the chromates used and therefore may be deducted from the total insoluble matter, thus affording the percentage of distinctly objectionable impurities, viz., metallic lead and red lead.

CHAPTER XXVI.

ANALYSIS OF PAINTS FOR MANUFACTURING PURPOSES.

499. Classification. Under the above heading is included an immense variety of paint products, the majority of which are sold in paste or semi-paste form, the thinning down being accomplished by the purchaser. The most common use is for agricultural machinery, such as harvesters, threshers, wagons, plows, etc., the paint usually being applied by the "dipping" process. A large amount of paints is used for bedsteads, refrigerators, etc. Considerable amounts of paint are used in the manufacture of toys, as primers for sashes and doors, for shade cloth, oilcloth, trunks, etc. Bridge paints, structural iron and steel paints, and paints for the railroad trade also form a very important class of paint products.

500. Analysis. The analysis of these various paint products offers no particular difficulties, and the schemes outlined in other chapters for the various colors will be found to be satisfactory in the majority of instances. Immense quantities of para reds, precipitated on various inert bases such as barytes, china clay, magnesium silicate, etc., are used in agricultural paints. The actual amount of para red used is the most important factor in determining the cost or selling price of such paints. The amount present can be determined approximately by difference, *i.e.*, by determining the combined percentage of inert materials and subtracting from 100. Unless the determinations are performed

with extreme care and discrimination, serious errors are liable to be made, and it is often advisable to check the analysis by a determination of the amount of para red present, which can be accomplished by determining the percentage of nitrogen by the Kjeldahl method, modified as for nitrates, as the diazo radical is so easily broken down that unless considerable care is observed a loss of nitrogen compounds will occur. The Kjeldahl method is given in full in the various published reports of the Association of Official Agricultural Chemists.

501. Presence of color lakes. If the color of the paint varies materially from that obtained with a straight para red, other organic colors, as eosine, Bordeaux B, Scarlet No. 1, etc., may be present, in which case the nitrogen determination is to a large extent valueless. For the detection of the different organic colors present the author has found the "Treatise on Color Manufacture," by Zerr, Rubencamp and Mayer, the most thorough and comprehensive of any yet published.

It should be remembered that while the principles underlying the manufacture of the para reds, so called, are well known, yet certain color makers are enabled to produce more brilliant and stronger reds than others; and in attempting to duplicate a manufacturing trade's paint containing a para red the question of inherent strength and brilliancy must be taken into consideration.

502. Analyses. The following analyses made in the author's laboratory show some of the combinations in use by the leading manufacturers of agricultural machinery implements, shade cloth, beds, etc.

VERMILION PRIMERS.

	I. Wagons. Per cent.	II. Seeding Machinery. Per cent.	III. Harvester Machinery. Per cent.
White lead	25.24	...	...
Zinc-lead white	...	27.86	...
Lithopone	...	...	60.62
Barium sulphate	5.80	15.18	...
Barium carbonate	...	52.74	...
Calcium carbonate	66.97	...	36.80
Iron oxide	...	...	1.25
Para red	1.99	4.22	1.33
	100.00	100.00	100.00

PRIMING ENAMEL—BEDS.

	I. Per cent.	II. Per cent.
Lithopone	49.04	63.37
Zinc oxide	2.60	22.50
Calcium carbonate	48.27	13.85
	99.91	99.72

WHITE BARREL PASTE.

	Per cent.
Zinc oxide	39.85
Calcium carbonate	60.15
	100.00

SHADE CLOTH, BODY WHITE.

	Per cent.
Lithopone	33.21
Silica	1.98
Calcium carbonate	64.51
	99.70

YELLOW AND GREEN PASTES—PLOWS, WAGONS, PUMPS, PLANTING MACHINERY, ETC.

	I. Wagon Primer. Per cent.	II. Wagon Finishing Coat. Per cent.
Lead chromate	10.75	34.00
Calcium carbonate	47.60	66.00
Barium sulphate	41.65	...
	100.00	100.00

YELLOW AND GREEN PASTES — PLOWS, WAGONS, PUMPS, PLANTING MACHINERY, ETC. — *Continued.*

	I. Yellow Wagon Paste. Per cent.	II. Yellow Pump Paste. Per cent.	III. Yellow Wagon Paste. Per cent.
Lead chromate	8.32	50.22	12.09
White lead	65.70	...	...
Zinc oxide	13.20	...	58.35
Calcium carbonate	12.78	49.78	29.39
	100.00	100.00	99.83

CREAM PASTE — HARVESTER.

	Per cent.
Lithopone	48.64
Calcium carbonate	48.79
Ochre	1.08
Chrome yellow	1.49
	100.00

	I. Green Paste — Farm Machinery. Per cent.	II. Green Paste — Wagon. Per cent.
Chrome green	2.83	20.01
Zinc oxide	36.89	...
Barium sulphate	8.67	39.85
Calcium carbonate	51.61	...
Aluminum silicate	...	40.14
	100.00	100.00

	I. Green Plow Paste. Per cent.	II. Green Plow Paste. Per cent.
Chrome green	5.00	4.92
Zinc lead	58.51	...
Barium sulphate	13.70	10.57
Calcium carbonate	22.79	84.51
	100.00	100.00

RED WAGON PASTES.

	I. Per cent.	II. Per cent.	III. Per cent.
Zinc oxide	12.05	...	7.35
Barium sulphate	42.00	...	37.80
Calcium carbonate	30.09	87.52	...
Aluminum silicate	...	2.45	...
Red lead	...	...	44.44
Para lake	15.86	10.03	10.41
	100.00	100.00	100.00

	IV. Per cent.	V. Per cent.	VI. Per cent.
Barium sulphate	50.25	...	9.52
Red lead	41.26	43.65	62.78
Calcium carbonate	...	51.38	23.66
Para lake	8.49 [1]	4.97 [1]	4.04
	100.00	100.00	100.00

[1] Includes eosine.

RED LADDER PASTE.

	Per cent.
Barium sulphate	72.37
Red lead	20.28
Para lake	7.35
	100.00

RED PLOW PASTE.

	Per cent.
Zinc oxide	11.15
Barium sulphate	44.35
Calcium carbonate	30.68
Para lake	13.82
	100.00

RED THRESHER PASTE.

	Per cent.
Zinc oxide	9.95
Barium sulphate	53.45
Calcium carbonate	20.20
Para lake	16.40
	100.00

RED SEEDING MACHINERY PASTE.

	Per cent.
Barium sulphate	17.10
Calcium carbonate	63.58
Red lead	12.80
Para lake	6.52
	100.00

503. Dipping paints. As previously stated, a large portion of the agricultural machinery and implement paints is applied by what is known as the dipping process, *i.e.*, the articles to be painted are dipped in large tanks of the thinned paint. It is obviously necessary that the pigments used should be carefully and thoroughly ground and of as non-settling a nature as possible. These features are of as much importance as the chemical composition.

CHAPTER XXVII.

COMPOSITION AND ANALYSIS OF FILLERS.

504. Under the heading of fillers are included *paste* and *liquid wood fillers*, *crack* and *crevice fillers*, *iron fillers*, and *rough stuff*. The composition and properties of these various fillers will be considered separately.

505. Wood fillers. The fact that many of the wood fillers on the market are of inferior quality is not due to lack of knowledge of the manufacturer but to the question of price. The pigment portion of a high-grade paste wood filler should consist of 70 to 80 per cent of a finely ground quartz, such as Bridgeport silica, which possesses a decided "tooth." The remaining portion, 30 to 20 per cent, may be a "toothless" silicate like the well-known F. S. A. silica. The addition of 1 to 2 per cent of powdered starch is also of material benefit. The vehicle should be composed of a good medium-drying oil Japan, raw linseed oil, and turpentine; water should be absent.

The cheapening of wood fillers is accomplished by using an inferior benzine-rosin Japan and a cheap white silicate in place of the crushed quartz silica, the former being obtained at about one-third of the cost of the latter. Sometimes white mineral primer may be added for cheapening. Besides the customary chemical analysis, a careful microscopic examination should be made in order to differentiate the silicas used, the crushed quartz silica being recognized by the characteristic wedge-shaped structure of the particles; the

fineness of the particles being regulated according to the nature of the wood to be filled, open-grained woods requiring a filler containing quite a percentage of comparatively coarse particles.

506. Tinted wood fillers contain small percentages of tinting colors such as ochre, bone black, burnt umber, Vandyke brown; golden oak being obtained with the aid of ochre, burnt umber, and Vandyke brown; light oak with the use of a little ochre only; dark and light antique with the aid of burnt umber; and walnut with the aid of an asphaltum black.

507. Transparent liquid wood fillers or surfacers for hard, close-grained woods usually contain only 16 to 20 per cent of pigment, which may be white filler (talcum), or better, a mixture of crushed quartz silex and white filler. The vehicle should be a light, quick, hard-drying kauri varnish with turpentine thinner. Kerosene-oil-and-water emulsions have no legitimate place in this class of goods, although often present. Instead of kauri varnish, a rosin-china wood-oil varnish is often used, but is apt to cause considerable trouble, as on sandpapering it will either dust or soften and roll up under the paper.

508. Crack and crevice fillers. The basis of this class of goods is usually powdered starch, raw linseed oil, benzine Japan, and naphtha, which affords a cheap, efficient paste for the purpose indicated.

The following formula is typical of this class of products:

Starch	100 lbs.
Raw linseed oil	3¾ gal.
Benzine drier	1½ gal.
Benzine	1½ gal.

509. Iron fillers. This class of paints is always sold in paste form and may contain a small percentage of

white lead or zinc lead, Keystone filler, white filler, silica, barytes, or white mineral primer ground in linseed oil and Japan. The low price at which these fillers are sold, 3 to 4 cents per pound, precludes the use of any large percentage of lead pigments.

510. Analyses. The following analyses indicate the nature of some of the iron fillers on the market:

	I. White. Per cent.	II. Black. Per cent.	III. Maroon. Per cent.
Barium sulphate	40.85	...	37.40
White lead	16.12	5.26	...
Calcium carbonate	43.03	...	...
Keystone filler	...	94.74	...
Ferric oxide	...	...	30.51 [1]
Silica and silicates	...	...	12.97 [1]
Calcium sulphate, hydrated	...	...	19.12
	100.00	100.00	100.00

[1] Evidently Princes' metallic and Indian red.

The vehicles were judged to be blends of grinding Japan, rosin-china wood-oil varnish, and a benzine drier.

511. Rough stuff. This product is somewhat similar to iron filler in composition, but it usually has a much higher lead content and therefore commands a better price. The pigment portion is usually white lead, Keystone or similar filler, and a small percentage of lampblack, bone black, or carbon black. The vehicle is also similar to that used in iron fillers, except that in the better class of rough stuff a fairly good grade of kauri varnish is used.

ANALYSES OF ROUGH STUFF.

	I. Per cent.	II. Per cent.
Keystone filler	73.18 [1]	76.24 [2]
White lead	26.82	23.76
	100.00	100.00

[1] Tint indicated presence of small amount of lampblack.
[2] Contained considerable magnesium silicate; white filler probably present.

CHAPTER XXVIII.

SHINGLE STAINS, BARN AND ROOF PAINTS.

512. Shingle stains. The manufacture of really high-grade shingle stains has been accomplished by only a very few paint firms, as the basis of success is the obtaining of the right kind of creosote oil. There are a number of creosote oils on the market which have been freed from naphthalene sufficiently so that the naphthalene will not separate out when chilled or when the prepared stain is subjected to cold weather; but it will be observed that such creosote oils will be low in the phenyloid or preservative bodies, and therefore will exert little preservative action toward the wood, or else the prepared stain changes color in the package. This is particularly noticeable with the greens; the change will begin within a few weeks after being prepared and continue until the color has gone over to a dirty brown. A close examination will show that this change is usually not due to the alteration of the chrome green, but to the precipitation of a tarlike substance which forms a coating over the chrome-green particles and destroys their tinting strength.

513. Examination. It is necessary, if a high-strength creosote oil is to be used, to refine it, which has been found to be financially profitable to only a few manufacturers, and who use all of their product in the preparation of their own goods. The paint chemist, therefore, should not accept a creosote oil from the distillation figures only, but should conduct a practical try-

out, noting any changes that may take place in a can of the prepared stain, for two to three months. The author has made numerous analyses of the leading brands on the market, but found very little similarity in the products examined. Some were simply cheap linseed-oil paints and much reduced with naphtha, containing no creosote oil at all, the majority contained varying amounts of a weak creosote oil, low in phenyloid bodies, possessing little preservative action.

514. The following analysis reduced to formula is representative of a medium-priced, fairly high-grade shingle stain:

Creosote oil	10 gal.
Solvent naphtha[1]	12 gal.
Paraffine oil	12 gal.
Linseed oil	2 gal.
Asbestine pulp	9 lbs.
Chrome green, C. P.	15 lbs.

[1] A commercial mixture of benzole, toluene, and xylene.

515. **Barn paints, roof paints, fence paints, etc.** The prices at which these paints are offered for sale preclude the use of high-grade materials such as should be used in first-quality house paints. They are, however, usually satisfactory for the purpose intended. The same methods of analysis as are applied to house paints are applicable to barn and roof paints. The latter, however, usually offer numerous complexities, and the analytical results obtained must be interpreted with care and discrimination. It is by no means uncommon for manufacturers who label their goods as to composition to include, under the term *Japan drier*, a large percentage of naphtha or of kerosene oil, and under the term *varnish*, various rosin, rosin-oil, cottonseed-oil, soya-bean-oil, and corn-oil preparations. The detection of these various oils is comparatively easy, but the deter-

mination of the amounts present, especially of the last four, is largely a question of judgment rather than of exactness.

516. Analyses. The following analyses made by the author are believed to be representative of the combinations on the market:

	I.	II.	III.	IV.	V.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pigment	47.1	44.5	44.0	15.1	42.7
Vehicle	51.9	55.5	56.0	84.9	57.3
	100.0	100.0	100.0	100.0	100.0
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Vehicle:					
Linseed oil	52.5	29.0	30.0	41.4	31.0
Rosin and rosin oil	...	26.0	30.0	...	21.0
Cottonseed oil	16.6	...	...	...	...
Water	12.1	...	...	16.2	...
Benzine	18.8	45.0	40.0	42.4	48.0[1]
	100.0	100.0	100.0	100.0	100.0

[1] Includes kerosene.

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pigment:					
Lead sulphate	...	18.24	...	...	...
Zinc oxide	...	19.76	...	...	...
Aluminum silicate and silica	15.96	2.35	31.81	...	20.37
Calcium carbonate	13.76	58.45	43.89	79.11	11.46
Calcium sulphate	...	...	...	...	53.62
Ferric oxide	70.28	...	24.30	...	14.55
Carbon	...	1.20	...	20.89	...
	100.00	100.00	100.00	100.00	100.00

CHAPTER XXIX.

ANALYSIS OF JAPANS AND DRIERS.

517. At the present time the terms "Japan" and "drier" are interchangeable and refer to the same line of products,—manganese linoleate, lead linoleate, resinate of manganese, resinate of lead, or mixtures of these compounds. Originally Japan contained a considerable quantity of dissolved resin, constituting a preparation that on drying gave a film of considerable hardness and lustre, but this distinction has largely disappeared. These compounds should not be confused with baking Japans, which represent an entirely different class of products and which will not be discussed at this time. Japans and driers are usually made by heating the oxides of lead and manganese or borate of manganese with linseed oil or the various resins, and dissolving the melted mass in turpentine, benzine or mixtures of both.

518. Determination of the drying salts. The salts generally used are

	Litharge,	PbO
	Red lead,	Pb_3O_4
	Oxide of manganese,	MnO_2
	Borate of manganese,	MnB_2O_4
occasionally	Zinc sulphate,	$ZnSO_4$
and	Zinc oxide,	ZnO.

Weigh 25 grams of the drier into a 250 c.c. Erlenmeyer flask and dilute with 25 c.c. of a mixture of equal parts of benzine and turpentine. Add 50 c.c. of dilute

hydrochloric acid (1.10 sp. gr.). Allow to stand 1 hour, shaking thoroughly at intervals of 10 minutes. Immerse the flask in a beaker of hot water, at a considerable distance from the flame. When the contents of the flask are hot, shake with a circular motion, avoiding undue pressure in the flask. Allow to stand until cool, so as to be sure that the drier has been wholly dissolved. Pour into a separatory funnel, draw off the aqueous layer into a casserole, wash the oil portion twice with warm water, adding the washings to the casserole and evaporate to dryness under the hood. Dissolve in dilute nitric acid with the aid of heat, filter into a 250 c.c. graduated flask and after washing thoroughly make up to the mark.

519. **Lead.** To an aliquot portion add 5 c.c. of dilute sulphuric acid and evaporate on the hot plate until white fumes of sulphur trioxide appear. Cool, add cautiously 50 c.c. of water, heat to boiling, cool slightly, and add 50 c.c. of alcohol. Allow to stand one-half hour, filter onto a Gooch crucible, wash with 50 per cent alcohol, dry, heat gently and weigh as lead sulphate.

520. **Manganese.** To an aliquot portion of the sample add 5 c.c. of sulphuric acid, dilute with 10 c.c. of water, and evaporate on the hot plate until all of the hydrochloric acid is expelled as shown by copious evolution of sulphur trioxide fumes. Cool, dissolve in about 25 c.c. of water and heat carefully with occasional shaking until all of the anhydrous sulphate of iron has dissolved. Transfer to a 250 c.c. graduated flask and add an excess of zinc oxide emulsion, obtained by mixing C. P. zinc oxide with water. Avoid a large excess, but sufficient to precipitate all the iron, so that on standing the solution begins to settle clear and some

zinc oxide can be seen in the bottom of the flask. Cool and make up to the mark. Transfer an aliquot portion to a beaker or flask and add an excess of a saturated solution of bromine water, and about 3 grams of sodium acetate. One c.c. of a saturated solution of bromine water will precipitate about 0.01 gram of manganese. Boil about 2 minutes. Filter and wash with hot water. The filtrate must be perfectly clear. Place the filter containing the washed precipitate back in the beaker or flask in which the precipitation was made. All traces of bromine must be entirely expelled.

Add an excess of standard oxalic acid solution and about 50 c.c. of dilute sulphuric acid (1 : 9) and heat nearly to boiling with gentle agitation until the precipitate is entirely dissolved. Dilute to about 200 c.c. with hot water and titrate with standard permanganate.

521. Zinc. Zinc sulphate and zinc oxide are but little used at present in driers. If present zinc may be estimated in the filtrate from the lead sulphate, as described under the analysis of mixed paints containing umbers and siennas.

522. Calculations. The color of the drier gives a clue as to the combinations used, borate of manganese being used in light colored driers, oxide of manganese in dark driers, and the oxides of lead in medium colored driers. By far the most common combination is a mixture of borate of manganese and litharge.

523. Determination of the volatile oils. Five grams of the drier are quickly weighed into a flat-bottomed dish (a petri-plate is the most suitable), dried for 3 hours at 150° C., cooled and weighed. Loss in weight represents very closely the amount of volatile thinner pres-

ent, and in the samples analyzed by the author the volatile thinners constituted 63 to 68 per cent by weight.

524. Separation of benzine and turpentine. About 100 grams of the drier are distilled to the point of incipient decomposition, the distillate redistilled and the benzine estimated by the Sulphuric Acid Number, as described under the analysis of volatile oils.

525. Detection of rosin. About 1 c.c. of the drier is dissolved in 15 c.c. of acetic anhydride, warming until the solution is complete. Cool, filter, place a few drops of the filtrate on a crucible cover and add a drop of sulphuric acid, so that it will mix slowly. If rosin is present a characteristic fugitive violet color results. Linoleate driers sometimes give a color resembling that of rosin driers, and it is better to evaporate a portion of the drier to a syrup consistency, treat with alcohol, and test the alcoholic extract.

526. Practical tests. The chemical analysis of a Japan will give very little information regarding its efficiency, since the latter is largely dependent upon the conditions of manufacture. The following specifications,[1] as adopted and used by the Philadelphia and Reading Railroad, give very excellent methods for determining the efficiency of a Japan.

"The material desired consists of a pure turpentine hardener and oil drier, conforming to the following:

1st. When equal parts by weight of the Japan and of pure turpentine are thoroughly mixed and poured over a slab of glass, which is then placed nearly vertical at a temperature of 100° Fahrenheit, with a free access of air, but not exposed to draught, the coating shall be

[1] Practical Testing and Valuation of Japan, by Robert Job, Chemical Engineer, Vol. IV., No. 5.

hard and dry, neither brittle nor sticky, in not exceeding 12 minutes.

2d. When thoroughly mixed with pure raw linseed oil at the ordinary temperature in proportions of 5 per cent by weight of Japan to 95 per cent by weight of raw linseed oil, no curdling shall result, nor any marked separation or settling on standing.

3d. When the above mixture is flowed over a slab of glass, which is then placed nearly vertical, at a temperature of 100° Fahrenheit, with free access to air, but not exposed to draught, the coating shall dry throughout, neither brittle nor sticky, in not exceeding 2 hours.

4th. When five cubic centimeters of the Japan are poured into 95 cubic centimeters of pure turpentine at the ordinary temperature, and thoroughly shaken, a clear solution shall result, without residue, on standing 1 hour.

5th. After evaporation of the turpentine, the solid residue must be hard and tough, and must not 'dust' when scratched with a knife.

6th. Benzine or mineral oil of any kind will not be permitted.

Shipments which are not closely in accordance with these specifications, or which are not of uniform quality throughout, will be returned at the expense of the shipper."

527. The temperature of 100° F. is obtained by the use of a suitable oven. The strips of glass used being 4 inches long by 2 inches wide. They are so placed in the oven that there is free access of air, but no draught. The bulb of the thermometer is placed beside the glass strips and the dryness of the film tested opposite the bulb of the thermometer.

The addition of rosin renders the dry film brittle and hence will "dust" when scratched with a knife.

The majority of driers used for house and barn paints are weak driers, and will not meet the above requirements. However, if the chemist will test out a few high-class driers by the above specifications, he will have but little trouble in estimating the value of the cheaper and inferior driers.

The United States Treasury specifications for manganese borate require that it be free from by-products, and that, other properties being satisfactory, preference will be given to the article containing the least amount of alkali.

Another practical test much in vogue among practical painters and shop foremen is to make a semi-paste with moisture-free litharge and the drier. High-class driers will remain three to four days before showing a decided tendency to thicken or harden; cheap rosin driers will begin to harden in a comparatively short time.

CHAPTER XXX.

ANALYSIS OF SHELLAC AND SPIRIT VARNISHES.

Analysis of Shellac.

528. The most common adulterant of shellac is common rosin or colophony. Sabin, in his Technology of Paint and Varnish, says that, "It is reported and probably true, that large quantities of common rosin are shipped to India and used as an adulterant of gum shellac."

529. **Detection of rosin.** About 1 gram of the sample is dissolved in about 15 c.c. of acetic anhydride, warming gently until the solution is complete. Cool thoroughly under the tap. The rosin will remain in solution while the greater part of the shellac will separate out. Filter. Place a few drops of the filtrate on a porcelain crucible, cover, and add by means of stirring rod one drop of sulphuric acid (34.7 c.c. sulphuric acid and 35.7 c.c. water) so that it will mix slowly. If rosin is present a characteristic violet fugitive color results. A pure shellac should give no coloration.

530. **Estimation of rosin.** The amount of rosin present is best estimated by means of the iodine number. For this purpose the Hanus method is to be preferred to the Hubl or Wijs method. The Hubl for a long time has been the official method, but it has several faults which affect its accuracy. It rapidly loses strength and is so slow in its reaction with some oils, such as linseed oil, that a serious error is brought about by

the change in strength of the solution during the reaction. Another objection to the Hubl method is that practically each chemist uses a modification of his own as regards the time necessary for the solution to remain in contact with the substance to be tested.

In their workings the Hanus and Wijs methods are very similar, but the Hanus solution is much easier to prepare and the results obtained more nearly correspond to those obtained by the Hubl method. As most of the published data relating to the iodine numbers of oils, fats, etc., has been obtained by the use of the Hubl method, this fact is of considerable importance in making comparisons.

531. The Hanus solution is prepared and used as previously described.

0.2 gram to 0.3 gram of the ground sample is introduced into a 250 c.c. Erlenmeyer flask; 20 c.c. of glacial acetic acid added, and the mixture warmed until the solution is complete, except for the wax. 10 c.c. of chloroform is added, the solution cooled to room temperature, and 25 c.c. of Hanus solution added, the flask stoppered, allowed to remain in the dark or in diffused light for 1 hour, with occasional shaking. 10 c.c. of potassium iodide solution and 100 c.c. of water are added and titrated with tenth-normal thiosulphate, using starch as an indicator in the usual manner. Blank determinations should be made each time.

EXAMPLE:

Wt. of sample = 0.4 gram.

A blank of 25 c.c of Hanus solution required 55 c.c. of thiosulphate.

1 c.c. of thiosulphate = .0125 gram of iodine. Titration of unabsorbed iodine = 49.5 c.c. thiosulphate.

55.0 − 49.5 = 5.5 c.c. of thiosulphate equivalent to iodine absorbed.

(5.5 × 100 × .0125) ÷ 0.4 = 17.2 per cent iodine absorbed.

532. Iodine Numbers of shellacs obtained from the leading wholesalers and jobbers of the United States, supposed to be strictly pure: [1]

No.	Variety.	Iodine No.	Color Reaction.[2]
1	Orange shellac	31.06	Rosin present.
2	Unbleached shellac	15.85	Rosin absent.
3	Orange shellac	12.68	Rosin absent.
4	Ralle standard shellac	16.80	Rosin absent.
5	Star brand shellac	14.90	Rosin absent.
6	H. N. superior shellac	12.99	Rosin absent.
13	Orange shellac	22.27	Rosin present.
14	Orange shellac	20.36	Rosin absent.
15	Orange shellac	16.54	Rosin absent.
16	Orange shellac	20.36	Rosin absent.
17	Orange shellac	13.36	Rosin absent.
7	Bone dry bleached shellac	8.87	Rosin absent.
8	Refined bone dry bleached shellac	12.34	Rosin absent.
9	Bleached shellac	6.34	Rosin absent.
10	Bleached shellac	8.87	Rosin absent.
12	Bleached shellac	13.36	Rosin absent.

Analysis of Shellac Varnish.

533. **Composition.** A varnish having the proper consistency is prepared by dissolving 45 parts of shellac in 55 parts of grain alcohol of 94 per cent strength or about 5 pounds of shellac per gallon of alcohol. In place of the expensive grain alcohol, some manufacturers substitute wood alcohol or Columbian spirits, which is rectified wood alcohol. The poisonous properties of wood alcohol are well known, and on account of its injurious effects great care should be exercised in the use of varnishes containing it. Shellac varnish

[1] Analyses by author.

[2] Libermann-Storch Reaction.

is often adulterated with rosin, thus producing a product of an inferior quality. The sophistication of varnish with this substance is well described by Langmuir:[1] "Starting out with an adulterated shellac, the varnish maker, secure in his belief that rosin cannot be detected in the solution, proceeds to add still more rosin. What has been said in regard to adulteration of shellac fades into insignificance in comparison with that practice in the manufacture of shellac varnishes. Shellac varnishes are sold containing no shellac. 'Pure' shellac varnishes, grain alcohol, may be purchased at less cost than the alcohol."

534. Determination of the body of shellac varnishes. 3 to 5 grams of the well stirred sample is weighed into a weighed flat-bottom petri-dish and evaporated to a constant weight in the steam oven. The result is calculated in pounds per gallon. If a platinum evaporating dish be used and the evaporation conducted over a water bath, the amount taken should not be over 1 gram. Taking the weight of a gallon of wood alcohol at 60° F. as 6.75 pounds, the pounds per gallon may be ascertained by means of the following table:[2]

Per cent. Residue.	Pounds per Gallon.
30.77	3.0
34.15	3.5
37.20	4.0
40.00	4.5
42.55	5.0
44.90	5.5
47.06	6.0
49.05	6.5
50.91	7.0
52.63	7.5
54.23	8.0

[1] Determination of Rosin in Shellac, J. Soc. Chem. Ind., January 1, 1905.

[2] Ibid.

535. Determination of the strength of the alcohol used. The strength of the alcohol may be calculated, knowing the per cent of residue as determined above and the specific gravity of the varnish. The calculation is best illustrated by the following example:

5 grams of varnish yielded a residue of 2.300 grams.

The specific gravity of the varnish was 0.9445 at 15.5° C.

100 grams of the varnish gave $2.300 \times 20 = 46.00$ grams of residue or 46.00 per cent.

The alcohol by difference $100.00 - 46.00 = 54.00$ grams or 54.00 per cent.

Average specific gravity of shellac itself = 1.145.

The volume taken up by the shellac in the varnish would be $46.00 \div 1.145 = 40.17$ c.c. in 100 grams of varnish.

The specific gravity of the varnish was 0.9445.

100 c.c. would weigh 94.45 grams and hence 100 grams would occupy 105.9 c.c.

105.9 c.c. − 40.17 c.c. = 65.73 c.c., the volume occupied by 54.00 grams of alcohol solvent.

$54.00 \div 65.73 = 0.8215$, the specific gravity of the alcohol. From the alcohol tables this will be found to correspond to 90.5 per cent of grain alcohol. If desired a portion of the varnish may be distilled until the decomposition point is reached and the strength of the alcohol determined from the specific gravity of the distillate.

536. Examination of the solvent. One hundred grams of the varnish are carefully distilled to the point of incipient decomposition. If necessary the distillate may be redistilled.

537. Detection of benzine. Dilute a portion of the

distillate with three or four volumes of water. If benzine is present it will separate out.

538. **Columbian spirit and wood alcohol.** The test for acetone, which is always to be found in wood alcohol, will distinguish between Columbian spirit and wood alcohol.

539. **Detection and estimation of wood alcohol in mixtures with grain alcohol.** Qualitatively, the methyl alcohol may be detected by the following method:

Dilute a portion of the distillate until the liquid contains approximately 12 per cent of alcohol by weight.

Oxidize 10 c.c. of the liquid in a test tube as follows: Wind copper wire 1 mm. thick upon a rod or pencil 7 to 8 mm. thick in such a manner as to enclose the fixed end of the wire and to form a close coil 3 to 3.5 cm. long. Twist the two ends of the wire into a stem 20 cm. long and bend the stem at right angles about 6 cm. from the free end, or so that the coil may be plunged to the bottom of a test tube, preferably about 16 mm. wide and 16 mm. long. Heat the coil in the upper or oxidizing flame of a Bunsen burner to a red heat throughout. Plunge the heated coil to the bottom of the test tube containing the diluted alcohol. Withdraw the coil after a second's time and dip it in water. Repeat the operation from three to five times, or until the film of copper oxide ceases to be reduced. Cool the liquid in the test tube meanwhile by immersion in water.

540. Add 1 c.c. of strong ammonia to the oxidized liquid in a casserole and expel the acetaldehyde by boiling gently over a direct flame until the vapor ceases to smell of ammonia. Add 2 to 3 drops of strong hydrochloric acid to set free the formaldehyde which has been retained as hexamethyltetramin, and bring the liquid momentarily to a boil; cool promptly

by immersion of the casserole in water and test for formaldehyde by the modified resorcin test, as follows:

Add to the liquid remaining 1 drop of a solution containing 1 part of resorcin in 200 parts of water, and pour the mixture cautiously into a test tube containing 3 c.c. of concentrated sulphuric acid, holding the tube in an inclined position in such a manner that the two liquids shall not mix. Allow it to stand 3 minutes, then sway the tube slowly from side to side in such a manner as to produce a gentle rotary motion of the two layers. Persist in this operation, if necessary, for a minute or more, using a piece of white paper for a background, and producing only a very gradual and partial mixing of the acid and water. Nearly half of the acid should remain as a distinct unmixed layer at the end. When methyl alcohol is present, the shaking causes the separation of more or less voluminous flocks of a very characteristic rose-red color. The appearance of colored zones or flocks of other hues, even when tinged with red, or of a rose-red solution without flocks, should never be considered proof of the presence of methyl alcohol. However, if the flocks are reddish brown, or if the upper layer has a pronounced red, it is often well to repeat the test.

By this method for the removal of acetaldehyde 10 per cent of methyl alcohol may be readily detected, and an experienced operator may detect with certainty a less amount.

541. Quantitatively the methyl alcohol may be estimated by the method of Thorp and Homes.

This method depends upon the fact that in the presence of potassium dichromate and sulphuric acid in a

closed vessel at 100°, ethyl alcohol is converted into its theoretical equivalent of acetic acid, while with methyl alcohol, the product resulting from the oxidation is always carbon dioxide and water. It has, however, been found that for each gram of ethyl alcohol present in the solution 0.01 gram of carbon dioxide may be formed and this correction should be made in all determinations.

The specific gravity is determined by means of a pycnometer. The total per cent of the alcohol is practically the same as the per cent of ethyl alcohol of the same specific gravity.

542. The methyl alcohol is determined by converting it into carbon dioxide by means of sulphuric acid and potassium dichromate in the Knorrs' apparatus described under the estimation of carbon dioxide in white lead.

Weigh into the flask 20 grams of potassium dichromate, connect the apparatus after having weighed the soda-lime tubes. Introduce through the stop-cock funnel an exact volume of the alcohols not to exceed 4 grams of the mixed alcohols, and an amount of water equal to 50 c.c. less the number of c.c. of alcoholic solution, 80 c.c. of sulphuric acid (made by diluting one volume of concentrated acid with four volumes of water) are added, well shaken and allowed to stand 18 hours. Dissolve 10 grams of potassium dichromate in 50 c.c. of water, add through the funnel, then add 50 c.c. of concentrated sulphuric acid and heat the contents of the flask to boiling for about ten minutes, the carbon dioxide being carried off by a current of air through the apparatus. The heat is now removed and the current of air continued for a few minutes longer. Disconnect and weigh the soda-lime tubes.

Calculate the methyl alcohol from the proportion

$$1.373 : 1 : : \text{wt. } CO_2 \text{ obtained} : x$$
$$x = \text{wt. methyl alcohol,}$$

the theoretical oxidation of 1 gram methyl alcohol producing 1.373 grams of carbon dioxide.

EXAMPLE.

Specific gravity of sample,	0.7992
Weight of sample used,	1.0118 grams
Weight of carbon dioxide,	1.3810 grams

$1.373 : 1 : : 1.3810 : x$

$x = 1.006$ grams methyl alcohol.

$1.0118 : 1.1006 : : 100 : y$

$y = 99.4$ per cent methyl alcohol.

543. If ethyl alcohol is present, the correction previously referred to, of 0.01 gram carbon dioxide for each gram of ethyl alcohol, should always be applied. The weight of the methyl alcohol subtracted from the weight of the mixed alcohols (calculated from the sp. gr.) gives the weight of the ethyl alcohol, approximately. The weight obtained by 0.01 gives correction to be deducted from the total carbon dioxide, for the recalculation of the weight of methyl alcohol. It is obvious that a very slight error is thus introduced, but the writer believes that it is so small that it may be safely neglected.

544. **Detection and estimation of rosin.** The residue remaining after the drying of the varnish in the determination of the "body" may be used for the detection of rosin as described under the examination of shellac.

If much rosin is present, it is not safe to take the residue after evaporation for the quantitative estimation as has been shown by Langmuir. "A little rosin

(iodine value 224.3) was dissolved in alcohol, evaporated on the water bath and heated 5 hours. It then showed a value of 148.2. Similarly, a dark rosin 175.7 fell to 131."

A quantity of the varnish sufficient to yield 0.2 to 0.4 gram of residue is weighed from a small vial, provided with a perforated stopper carrying a shortened 1 c.c. pipette, into a 200 c.c. Erlenmeyer flask; the weight of the sample used being thus obtained by difference. The sample in the flask is carefully evaporated at a low temperature until pasty and then dissolved in the requisite amount of acetic acid and chloroform and the iodine number then determined in the usual manner. The error due to the action of the small amount of alcohol remaining in the pasty mass on the thiosulphate is negligible.

In calculating the per cent of rosin the iodine values of 150 [1] for rosin, 16 [1] for unbleached and 11 [1] for bleached shellac may be used. If other resins are present, as sandarac, etc., these can only be calculated in the terms of rosin.

545. Estimation of rosin, Mannhardt's method.[2] Five grams of gum shellac or 10 grams of shellac varnish are weighed into a casserole flask, and the solvent expelled on the water bath. The residue is saponified with alcoholic potash, the alcohol expelled, and the residue taken up in 100 c.c. of hot water. At this point any wax present may be extracted with benzine (sp. gr. 730), the benzine evaporated off, and the residue weighed.

The solution of the soaps is treated with 50 c.c. benzine (sp. gr. .730), shaken vigorously, and, before the

[1] Average values obtained by author.

[2] Hans Mannhardt, Chemist, Heath & Milligan Mfg. Co.

emulsion has time to separate out, add dilute sulphuric acid in slight excess. The shellac acids immediately coagulate, and all rosin acids go into the benzine, which is readily separated, filtered and evaporated in a weighed beaker. The shellac acids are absolutely insoluble in benzine. Damar and possibly sandarac will behave like rosin.

546. **Practical test for brewers' varnish.** Varnishes for brewers' purposes should be made from pure shellac and grain alcohol 94 per cent strength. They may be tested out by varnishing a strip of wood 6 inches long by 3 inches wide, and a quarter of an inch in thickness, and after drying immerse half of the strip in 4 per cent alcohol for 48 hours. A varnish made from impure shellac or alcohol of less than the proper strength will soon turn white.

547. ANALYSES OF SHELLAC VARNISHES.[1]

No.	Variety.	Iodine Number.	Percentage of Gum.	Calculated Percentage Rosin.
18	Orange shellac.	40.5	49.8	18.3
19	Orange shellac.	13.4	42.2	....
23	Orange shellac.	26.2	37.1	7.6[2]
25	Orange shellac.	16.2	35.9	....
26	Orange shellac.	15.2	21.0	....
27	Orange shellac.	37.4	13.3	16.0
29	Orange shellac.	23.3	40.5	5.4[2]
31	Orange shellac.	15.0	39.8	....
20	White shellac	40.8	44.1	21.4
30	White shellac	37.8	22.4	19.3
21	White shellac	13.3	41.0	....
22	White shellac	16.2	37.6	....
28	White shellac	17.5	42.0	....

[1] Analyses by author.

[2] Liebermann-Storch reaction produces a somewhat different color than that usually given by rosin, hence these samples may be adulterated with other gums.

548. **Damar varnish.** The following specifications adopted by the Navy Department, May, 1904, will

serve for the practical testing and valuation of damar varnish.

Damar varnish must be made from the very best quality of damar gum in a solution containing at least 50 per cent of gum and 45 per cent of turpentine, the gum to be digested cold and well settled. The varnish must be as clear as and not darker than the standard sample, and must be free from benzine, rosin, lime, or other mineral matter. Its specific gravity at 60° F. must be about 0.950, and its flash point between 105° and 115° F. It must set to touch in not more than 20 minutes, and when mixed with pure zinc oxide must show a smooth, glossy surface equal to that shown by the standard sample.

549. **Tests.** Besides chemical tests to determine the above qualities, and practical tests to determine its qualities of finish, a board properly coated with a mixture of zinc and the liquid will be exposed to the weather for a period of 1 month, and at the end of this time must have stood exposure equally as well as the standard sample. A similarly prepared sample will also be baked at 250° F., and must not at this temperature show any greater signs of cracking, blistering, or any other defects than standard samples under the same conditions. Another sample, similarly prepared, will be exposed in a dark room at ordinary temperature for a period of 1 month and at the end of this time must not have turned darker to any appreciable degree than the standard sample.

CHAPTER XXXI.

ANALYSIS OF OIL VARNISHES.

550. Analysis of oil varnishes. As stated by Hurst, "The analysis of oil varnishes is one of great difficulty, as it is quite impossible to separate all the ingredients from one another." However in spite of the unsatisfactory state of our present knowledge of varnish analysis, a distillation and separation will give an approximate idea of the quantity and kind of volatile solvents used. Treating the residue by Twitchell's method, will give approximately the amount of oil and the amount of gum present in the varnish and an examination of the physical and chemical properties of the separated gum may give an approximate idea of its hardness, and throw some little light on its probable source. The presence of lime, color produced by the Liebermann-Storch reaction, acid figure and iodine absorption will indicate the presence of rosin and to some extent the amount present. With these tests, in conjunction with the solubility of the separated gum, the original character of the varnish, e.g., the pouring of a portion of the sample on a sheet of glass, noting how it flows, dries, the kind of film produced, its resistance to abrasion, to moisture, its elasticity, etc., and a comparison made with varnishes of known composition and similar properties, a very shrewd guess can be made as to how the varnish under consideration must be duplicated, or in other words, the approximate amounts of the different gums required to produce a similar product.

551. On the other hand, a proximate analysis of a varnish furnishes us with but a small amount of helpful information, as the gloss, working qualities, and durability depend largely on the quality of gum used, the quality and treatment of the oil, the quality of the driers used, and especially as to how the varnish was prepared, as regards heat, method of cooking, ageing, filtering, etc. On these essential points a chemical analysis tells us but little. That greater light will eventually be thrown on the problems involved, the author has not the slightest doubt, but meanwhile interpretations based solely on chemical analyses are liable to be more or less misleading; but taken in connection with physical tests, carefully made, the value of varnishes can be determined with considerable accuracy.

552. **Specific gravity.** The determination of the specific gravity is of considerable importance and should be made with a pycnometer at 15.5° C.

553. **Viscosity.** The determination of the viscosity of a varnish will throw considerable light on its working qualities. Any of the standard types of viscosimeters may be used for varnish work, but the Doolittle Torsion Viscosimeter offers several advantages over the others.

554. **Separation, identification, and estimation of the volatile oils.** Seventy-five grams of a uniform sample of the varnish is weighed into a 500 c.c. distilling flask, provided with a tube leading very nearly to the bottom, the other end of which is connected with a steam supply. The flask is also provided with a thermometer, the bulb of which dips below the surface of the varnish, and the flask then connected with a rather long condenser. By means of an oil bath the varnish is heated to 130° C., and a current of steam passed

through, until about 500 c.c. of water has passed over, or until the steam ceases to carry over any more volatile oil. It is advisable to collect the distillate directly in a separating funnel. When the volatile oil has completely settled out, the water is drawn off and the oil transferred to a weighed flask, weighed, and the percentage calculated. The aqueous distillate will contain a small quantity of the volatile oil equal to about 0.4 gram per hundred c.c. This correction should be made in calculating the percentage.

The constituents of the volatile oil and the amount of petroleum products present may be determined in the same manner as in mixed paints."

555. **Separation of the resin gums from the oil, Twitchell's method.** The flask containing the residue of oil and gum is connected with a return condenser, 150 c.c. of normal alcoholic potash added, the flask heated carefully on a water bath to avoid bumping and finally heated over a free flame for about an hour. The solution is then cooled and separated from the residue, which is again treated with alcoholic potash, and the process continued until as complete a saponification as possible has been made; usually a small residue of about 1 per cent remains. The different alcoholic solutions are united, neutralized with hydrochloric acid, the excess of alcohol evaporated off, and the fatty acids and gums removed with successive portions of ether. The ethereal solution is distilled to remove the ether, a small quantity of absolute alcohol added, and the flask again heated gently, the alcohol carrying off the last traces of water. About 10 volumes of absolute alcohol are added to the dry gums and acids, the solution being kept cold by ice and dry hydrochloric acid gas is passed in until the solution is sat-

urated. This will usually take from 30 to 45 minutes. The flask and contents are allowed to stand for about an hour, then diluted with about 5 volumes of hot water, and boiled until clear; the heating being conducted gently to avoid frothing.

556. The contents of the flask are mixed with a little petroleum ether, boiling below 80° C., and transferred to a separating funnel, the flask being washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off and the petroleum ether layer washed once with water, and then treated in the funnel with a solution of 2.5 grams of potassium hydroxide and 20 c.c. of alcohol in 200 c.c. of water. The ethylic esters dissolved in the petroleum ether will then be found to float on top, the rosin acids having been extracted by the dilute alkaline solution to form rosin soap. The soap solution is then run off, decomposed with hydrochloric acid, and the separated rosin acids collected as such, or preferably dissolved in ether, and the whole evaporated in a small weighed beaker on the water bath. A small quantity of absolute alcohol is added, and the evaporation repeated. Finally, cool in the desiccator and weigh. This will give approximately the amount of gums present in the varnish. Any residue insoluble in the 10 volumes of absolute alcohol above mentioned is weighed up and its weight added to the weight of resin gum.

557. **Separation of the gums from the oil, Scott's Method.**[1] In separating the gum, by this method, it is necessary to know whether the sample is a Long Oil or Short Oil Varnish, i.e., whether it contains a large or small amount of linseed oil. Hard oil finishes, inte-

[1] Drugs, oils, and paints, XV., No. 4, page 132, and No. 6, page 219.

rior varnishes, and rubbing varnishes are usually short oil varnishes, while carriage and similar varnishes are long oil varnishes.

In order to determine to which class a varnish belongs, about 10 c.c. of the sample is poured into a beaker and 50 c.c. of benzine, previously cooled to about 5° C., added. If the sample be short oil varnish the gums will be partially precipitated, while a long oil varnish will show but little change. The color of the precipitated gum may be considered as another indication, a light colored precipitate denoting a short oil, and a dark colored precipitate, a long oil varnish.

558. **Short oil varnishes.** A beaker of about 150 c.c. capacity, provided with a stirring rod, is carefully weighed, and about 10 grams of varnish weighed into it. Cool to below 10° C. Fifty c.c. of petroleum ether that has previously been cooled to below 3° C. is poured into the beaker and the contents stirred. The beaker is placed in a freezing mixture for about an hour, or until the precipitated gums have settled.

559. Place a filter paper that has been dried in the oven, in the suction funnel. Moisten and suck the filter free from surplus moisture, pour in the gasoline, retaining as much of the resins as possible in the beaker. Add another 50 c.c. of ice cold petroleum ether, and allow to stand as before on the freezing mixture. Meanwhile pour 25 c.c. of ice cold water on the filter paper, allowing it to run into the petroleum ether filtrate, which is then vigorously shaken up so as to thoroughly mix the water and petroleum ether, which causes the gum held in solution by the ether to precipitate, and on refiltering is retained. The second ether solution that has been cooling is now poured on to the filter along with the precipitate, rins-

ing out the beaker with ice cold petroleum ether. Treat with 25 c.c. of ice cold water, shaking and refiltering, as described above. Repeat this operation twice, transfer the filter, and precipitate to the weighed beaker, and dry in the hot air oven at 105° to 115° C. and weigh. Increase in weight, over that of the beaker, stirring rod and filter, represents the weight of the gum.

The petroleum ether solution containing the varnish oils is poured into a weighed beaker, the excess of petroleum ether evaporated off with due precautions, and the beaker placed in the hot air oven for 3 hours at 150° C., cooled and weighed. The residue represents the fixed oils in the varnish.

560. **Long oil varnishes.** Distil off the thinners from a portion of the sample. Weigh out 10 grams of the gum and oil into a weighed beaker as described above, cool down below 15° C. and add 50 c.c. of petroleum ether cooled below 0° C. Set in the freezing mixture for an hour and finish exactly as described under short oil varnishes. The separation of the total gum in long oil varnishes is quite difficult and requires considerable patience and experience. According to the experience of the author, Scott's method gives somewhat low results, especially as rosin is quite soluble in cold petroleum ether.

561. **Determination of the so-called insoluble and soluble gums.** This method is somewhat similar to the above, and, in the hands of a careful chemist, when run alongside of standard varnishes, will throw considerable light on the nature of the sample in question.

Weigh 2 grams of the sample into a weighed 6-oz. wide-mouth flask, add 2 c.c. of chloroform, 100 c.c. of 80° petroleum ether, gradually and with constant shak-

ing so as to avoid any precipitation, until 15 c.c. are added, allow to stand over night. The precipitated gums adhere to the bottom of the flask. Decant and wash with a little petroleum ether. Dry to constant weight as insoluble gum.

The petroleum ether extract should be decanted into a weighed beaker, the petroleum ether evaporated off and the beaker dried at 100° for seven to eight days to constant weight. All linseed oil should now be in the form of linoxyn. Digest over night with chloroform, which will dissolve the gum, and leave the linoxyn undissolved. Filter through cotton wool. Evaporate off the chloroform, dry to constant weight in the steam oven and weigh as soluble gum.

A varnish to meet with the requirements of the United States Treasury Department, among other things, should contain not less than 25 per cent of best quality imported gums, and must not contain rosin or petroleum products.

Varnishes containing wood oil are liable to give misleading results by the above method, as the whole or a considerable portion of the wood oil will be precipitated by the petroleum ether, depending on the length of time and temperature to which the oil has been heated.

562. Detection and estimation of rosin in varnishes. Qualitatively rosin may be detected as follows: Pour about 5 c.c. of the varnish into a small separatory funnel, add about 5 c.c. of carbon bisulphide, shake and add 10 c.c. of acetic anhydride. Allow to stand until complete separation takes place. Draw off the lower layer, which is the acetic anhydride. Pour 1 or 2 c.c. of the acetic anhydride portion into an inverted crucible cover, add carefully, by means of a stirring rod, one drop of sulphuric acid (34.7 c.c. of sulphuric

acid to 35.7 c.c. of water) to the edge of the cover, so that it will mix slowly with the acetic anhydride, if rosin is present a characteristic fugitive violet color will result.

563. The quantitative estimation of rosin in the presence of other varnish gums is a problem of especial difficulty. Gill,[1] suggests a method based on comparative ester values. The ester value being obtained by subtracting the free acid value from the saponification value. The gums are separated from the oils by Twitchell's method, the last traces of moisture being removed by drying over sulphuric acid. Gill obtains the following values for rosin and kauri.

Gum.	Saponification.	Free Acids.	Ester.	Average.
Pure rosin, No. 1	182.3	160.1	22.2	....
Pure rosin, No. 6	185.7	161.7	24.0	23.1
Kauri, No. 1	124.2	41.0	83.2	....
Kauri, No. 2	129.7	45.0	84.7	84.0

By the use of the usual formula

$$x = \frac{100\,(I - n)}{m - n}$$

the percentage of adulteration may be approximated, as described in the chapter on the Analysis of the Vehicle, in discussing cotton-seed oil.

564. Gill's method is open to considerable criticism, as he directs that the Free Acid Value be obtained by direct titration, and the Saponification Value by saponifying in practically an open flask. Dietrich[2] has shown that direct titration gives acid values far too low for all resin, because the complete neutralization

[1] J. Amer. Chem. Soc., XXVIII., No. 12, page 1723.

[2] Analyse der Harze, Balsane, und Gumminharze.

of the rosin acid proceeds slowly. As an illustration of this point, Worstall [1] gives the following experiment.

"Several portions of a sample of kauri, whose acid number has been accurately determined as 103, were weighed out and the acid number determined by indirect titration at different intervals of time. The results were as follows:

Time.	Acid No.
5 minutes	82
1 hour	92
3 hours	96
6 hours	101
12 hours	102
18 hours	103

565. Regarding open saponification Worstall states that "from the researches of Tschirch and his pupils, it appears that the copals consist of 'resenes' — neutral compounds containing oxygen and possibly of an aldehyde nature — and of the resin acids. Other investigators have noted the fact that the copals will absorb oxygen, and evidently the increase in acid number and decrease in iodine absorption is due to the oxidation of these 'resenes,' by contact with the air, to resin acids. . . . That this increase in the acid number is actually due to oxidation, the following experiments will illustrate:

"A number of samples of Kauri were selected, each one finely powdered, and its acid and iodine numbers determined. These samples were then left four months in open bottles exposed to the air, and the powdered resins stirred from time to time to promote oxidation. At the end of this time their constants were again determined with the following results.

[1] Chemical Constants of Fossil Resins, J. A. Chem. Soc., XXV., page 860.

No.	Before Acid.	Oxidation Iodine.	After Acid.	Oxidation Iodine.	Acid Increase.	Iodine Decrease.
1	72	154	87	133	15	21
2	76	159	111	121	35	38
3	77	140	93	115	16	25
4	72	170	107	110	35	60
5	97	109	104	99	7	0
6	105	113	109	112	4	1

"Samples 1, 2, 3 and 4 were hard, 'bold' gum of highest quality, while samples 5 and 6 were of a soft, spongy, lowest grade Kauri, in which oxidation had already made much progress before the experiment was carried out.

"This oxidation proceeds rapidly in presence of alkalies, so that open saponification with alcoholic caustic potash gives acid numbers that are much too high. Doubtless this fact, in connection with the impossibility of obtaining correct acid numbers by direct titration, has led to the reporting of ester values in resins where no esters exist. That Kauri is free from esters was shown by saponifying several samples in flasks with return condensers, digesting for one hour on the steam bath. In every case the saponification number thus found was the same as the indirect acid number."

566. From the above data it is evident that, in order to approximate the percentage of rosin in a varnish by the so-called ester values according to Gill's method, each analyst must establish his own set of figures, under certain definite working conditions, obtaining his data from varnishes of known composition. Any variation of these conditions, either in time, factor or condition of the gums, is certain to give different results.

Little that is reliable has been written concerning the detection of the other varnish gums. Certain

resins, however, give some indication of their presence. For instance, Kauri imparts a reddish stain to a varnish. Damar, if present in considerable quantity, can be detected by its smell, especially in the dried varnish. It is seldom found in varnishes intended for outside use.

567. In closing, a word should be said concerning wood oil. This product, the properties of which are but little understood by the majority of chemists, is finding a wide use among varnish manufacturers. It is claimed by varnish manufacturers that by the use of wood oil, varnishes containing a large amount of rosin may be prepared, possessing satisfactory wearing qualities and free from the objectionable features of ordinary rosin varnishes. However, in light of the rather heavy losses encountered by a number of varnish firms in endeavoring to prepare a satisfactory rosin-wood oil varnish, the above claims of the varnish manufacturers may be questioned somewhat. As to the analysis of this type of varnish the author is not aware of any suitable published method. It is said, however, that it may be detected qualitatively by practical varnishers, in quantities as low as five per cent by the characteristic odor given off in sandpapering a coat which has barely dried.

568. Navy specifications for interior varnish for naval vessels, 1906. To be of the best quality and manufacture and equal in all respects — including body, covering properties, gloss, finish and durability — to the standard samples in the general storekeeper's office, navy yard, New York. To be made exclusively from the best grade of hard varnish resins, pure linseed oil, pure spirits of turpentine and lead manganese driers, and to be free from all adulterants or other foreign

materials. The varnish must flash above 105° F., set to touch in from 6 to 8 hours, and dry hard within 24 hours in a temperature of 70° F. It must stand rubbing with pumice stone and water within 36 hours without sweating, and must polish in 72 hours with rotten stone and water. To be as clear and not darker than the standard sample, and to be equal to it in all respects as above specified.

569. Navy specifications for black asphaltum varnish, 1906. Black asphaltum varnish must be of pure, high-grade asphaltum of the very best quality, pure linseed oil, pure spirits of turpentine and lead manganese driers, and to be free from all adulterants or other foreign materials, and must contain not less than 20 gallons of prepared linseed oil to 100 gallons of varnish. It must not flash below 105° F. (open tester). It must mix freely with raw linseed oil in all proportions; must be clear and free from sediment, resin, and naphtha, when flowed on glass, and allowed to drain in a vertical position; the film must be perfectly smooth and of full body. It must set to touch in from $1\frac{1}{2}$ to 2 hours, and dry hard in less than 20 hours at 70° F. When dry and hard it must not rub up or powder under friction by the finger. The application of heat must quicken the time of drying and give a harder film.

CHAPTER XXXII.

THE PRACTICAL TESTING OF VARNISHES.

570. The thorough practical testing of varnishes is an exceedingly difficult matter for the average chemist, as it requires long familiarity with the direct application of varnishes under a large variety of circumstances and conditions. However, there are several practical tests which can be made without special difficulty, and which will throw considerable light on the character of the varnish, especially if the chemist be supplied with a standard set of varnishes which he can run along with the sample to be tested, and have constantly by him to enable him to check up his judgment by comparison.

571. **Smell.** The smell of a varnish will often tell much concerning its value. A good, wholesome, gummy odor usually indicates a varnish made from good materials, while a strong, raw, pungent odor is often the sign of a cheaper grade of goods. Markedly inferior articles can almost without exception be detected in this manner. Occasionally the true odor of the varnish is masked by a strong turpentine odor, in which case allow a sample of the varnish to drain out of a beaker for 3 to 5 minutes and then note the smell of the portion adhering to the sides of the beaker, i.e., the "after smell," as it is called.

572. **Consistency.** The consistency of a varnish is to a considerable degree regulated according to the work for which it is to be used, and should be judged

accordingly. There is a marked tendency, at the present time, to make varnishes altogether too thin. This may in part be due to the insistent demands made by contractors and other varnish users for goods that will "work fast" and dry quickly, but it should be remembered that such varnishes do not afford the measure of protection to the surface that is regarded necessary by the best practical users of varnish.

573. **Working and flowing.** The working qualities of the varnish under the brush will at once show whether the chemist is dealing with a "long oil" or a "short oil" varnish. A test board having been suitably surfaced and filled either with thin shellac, or with the varnish reduced with 25 per cent of turpentine, dried and sandpapered down smooth, is given an even, uniform coat of the varnish to be tested. The length of time the varnish can be worked under the brush, before it exerts a characteristic "pull" on the brush, is indicative of the character of the varnish. If it permits of sufficient time for thorough brushing out so that a large panel could be coated and worked out smooth, before it begins to pull on the brush, i.e., "set up," the sample would be considered a long oil varnish, while if it begins to pull under the brush almost at once, it would be considered a short oil varnish. Naturally, there are varnishes which do not exhibit these extremes, but usually the classification can be made without difficulty.

574. Special notice should be taken of the way the varnish flows out into a uniform surface, whether it does so with ease, or slowly and with difficulty. In applying the final coats the working and flowing can be studied with greater exactness. Some varnishes will work easily, others will work "tough," some

"greasy," etc.; with a little experience the chemist can grade them with considerable accuracy. As mentioned in a preceding paragraph, there are many varnishes on the market which are altogether too thin. Such varnishes will work and flow with great ease because of their excessive thinness, and hence the consistency must be taken into account when passing on the working and flowing qualities.

575. Time of drying. The time a varnish requires to dry properly, i.e., to harden thoroughly, is regulated according to the purpose for which the varnish is to be used. For instance, floor varnishes are supposed to dry hard over night, while the average spar varnish will require a much longer time. Hence the samples tested should be compared with the accepted standards of those types of varnishes, both on the wood test surface and on a sheet of glass, on which samples of the varnishes have been placed and then set in a dust-free but unconfined place at an angle of about 30 degrees from the perpendicular. The best results are secured by resting the glass on a couple of small hooks, which permits the varnish to drain freely. The rapidity of the drying should be noted at regular intervals. When dry, the tests should be saved for further examination.

576. The sponge test. After the requisite number of coats have been applied to the test boards and the finishing coat has hardened thoroughly, a sponge made of several thicknesses of felt is thoroughly moistened and laid on the varnished surface and allowed to remain for a stated number of hours undisturbed. A high-grade varnish will either show no discoloration at all, or will regain its color on drying, provided, of course, that it has been suitably applied. A varnish containing a large amount of rosin will be more or less

badly corroded, and will remain permanently white and discolored. With a little practice by working with varnishes of known composition the chemist can make a pretty shrewd guess as to the approximate amount of rosin present by the degree of discoloration. Right here the author wishes to state that the use of cheap inferior rosin varnishes has caused untold damage. There is probably more rosin varnish sold than all other grades put together. It is claimed by high-class manufacturers that the addition of three or four per cent of hardened rosin will enable the varnish maker to melt his gums at a somewhat lower heat and without darkening, thus making a better and lighter-colored varnish; but the addition of rosin has passed this point so far that a three or four per cent addition is a very minor consideration indeed.

577. Another modification of the above test is to varnish a clean strip of tin, and after thorough drying immerse it under water and note the rapidity and extent of corrosion and discoloration.

578. **Toughness and elasticity.** In order for a varnish to be durable and give entire satisfaction, it must have the desired toughness and elasticity as well as the requisite hardness. A varnish which is brittle, although it may have the required hardness, will be easily cracked or crushed by a very moderate blow. Some varnishes are required to be tougher and more elastic than others, as in the case of floor finishes.

579. The varnish having thoroughly dried on the test glass alongside of the standard sample, its toughness may be determined to a certain extent by its behavior under the thumb-nail, and the results obtained compared with a similar examination on the varnish test board. Also the films of the thoroughly dried

varnish on the test glass may then be scratched with a sharp instrument. A small, sharply pointed knife-blade is excellent for this purpose. A first-class varnish having suitable toughness and elasticity will show a smooth, even scratch, no scaling or "dusting" being observable; and if the knife be held in the proper position, a small, uniform, coherent ribbon of varnish will be ploughed off. If the varnish is deficient in elasticity and toughness, it will scale away under the knife-point, exhibiting a ragged, irregular scratch. Varnish films containing rosin when tested with the knife-point will usually "dust" more or less badly, i.e., fly away from the knife-point in the form of a fine powder, settling on the glass at a considerable distance from the scratch. The fact that varnishes vary greatly in consistency should be taken into account in making these tests, as the films on the glass will vary in thickness according to the consistency of the varnish.

580. In judging the brittleness of a varnish on a test board, especially if it is hardwood, the effect of the material used for the first coat must be taken into consideration. This may be readily shown by taking a hardwood board, coating a portion of it with shellac, another portion with an average cheap liquid filler, and the remaining portion with the varnish itself. After applying two coats of varnish over the entire surface and allowing it to harden thoroughly, it will be found on testing the surface with a knife that the varnish over the liquid filler is very brittle, that over the shellac somewhat brittle, while the straight varnish-filled surface will remain tough and elastic. Another method of testing the elasticity is to varnish a strip of tin, and, after thorough drying, bend the tin and note the extent which the varnish gives under the strain to

which it is subjected. In making these various tests, the chemist must be certain that the varnish is thoroughly dry, as many of the cheaper varnishes harden slowly, and, if examined too soon, will show greater toughness and elasticity than would be obtained in actual practice.

581. Hardness. A varnish may have the toughness and elasticity required of first-class goods, but may be deficient in hardness. In order to report on the hardness, the chemist should have some means of giving this quality a numerical value. An instrument for this purpose has been devised by Dr. A. P. Laurie and F. G. Baily of Heriot Watt College, Edinburgh, the essential features of which are a central rod sliding easily in a vertical direction through holes in two brackets. The upper portion of the rod has a screw thread, on which is a running nut. By means of a milled head at the top the rod is twisted round, and the nut caused to travel up and down on the thread. A spring is attached at its upper end to the travelling nut at the lower end to the lower bracket. To the lower end of the rod is attached a hardened blunt steel point, and the varnished plate to be tested is placed under this point, and the point brought to the surface of the varnish. The test surface is drawn slowly under the point, the pressure being increased until a white scratch is observed, at which point the reading is noted on the scale. The machine reads to a maximum of 2000 grams. Spirit varnishes break down at a pressure of about 100 grams, rosin varnishes 200 to 400 grams, fairly good common varnishes at about 700 grams, and fine carriage varnishes at 1200 grams and upwards. The inventors claim that the best oil varnishes take twelve months to reach their maximum

hardness, and that the rate of drying and the ultimate hardness can be measured with accuracy by their instrument.

582. Classification of varnishes. The varnish industry has from its beginning been conducted with as much secrecy as possible, and but little has been published that would enable the average chemist to pass judgment on the different grades and varieties of varnish, and for this reason a short discussion of some of the principal classes of varnish may not be amiss.

583. Floor varnishes. Goods of this class should have a medium consistency. If heavy they will require a longer time to dry and harden than is desirable, and would be apt to become marred from usage before thoroughly hardened; if too thin they will not afford the desired protection to the wood. In price they are about the same as for first-class interior varnishes, ranging usually from $2.00 to $2.50 per gallon wholesale. Floor varnishes are usually "long oil" goods, as a high degree of elasticity is required.

584. Interior varnishes. Varnishes for interior work should be of fairly heavy consistency, so as to stand rubbing. For the best class of work they should be "long oil," although "short oil" goods may be used for the undercoats. In price they usually range from $2.00 to $2.50 per gallon wholesale. Often, especially in contract work, "No. 1 Coach" goods are used. This term means absolutely nothing, as it stands for no specific grade or quality of varnish. Sold under this name varnishes are put on the market for $0.90 to $1.10 per gallon, or even less, and are usually high in rosin and benzine or heavier petroleum-products. Polishing varnishes, such as are used for pianos, high-class furniture, etc., are usually of excellent quality,

averaging in price from $2.50 to $2.75, although the very best grades may run as high as $3.50 wholesale.

585. Interior varnishes being subjected to less strenuous usage than floor finishes, carriage or exterior goods, the tendency has been to lower the standard of quality, until perhaps low-grade, inferior goods are the rule, and really high-grade finishes the exception, on the market at the present time. Neither is the size of the company any guarantee that the product is of high value, for many of the best grades of varnishes are made by small concerns who depend on the quality of their goods rather than on extensive advertising for their sales.

586. **Exterior varnishes.** These should always be "long oil" goods. Spar varnishes, which are the usual type of exterior varnishes, should be of medium consistency, tough and elastic, and not easily scratched. In price they usually range from $3.00 to $3.75 per gallon wholesale. Carriage varnishes bring the highest price of all varnishes, and their successful manufacture is accomplished by only a comparatively small number of concerns, and but few domestic brands are rated equal to the best imported English goods. Domestic carriage varnishes range from $4.75 to $5.75 wholesale, and the best imported English goods at about $7.25 per gallon.

587. **Short volume.** It is a lamentable fact that varnish manufacturers almost invariably defraud the consumer by putting out their packages short in volume. Of eleven samples purchased by the author on the open market, in the original package none were full measure. The amount of shortage is given in the following table:

No.	Description.	Per Cent Shortage of Contents.
1	Floor Varnish	3.2
2	Floor Varnish	4.2
3	Floor Varnish	2.1
4	Interior Varnish	3.2
5	Exterior Varnish	2.1
6	Coach Varnish	2.1
7	Interior Varnish	8.4
8	Floor Varnish	3.2
9	Exterior Varnish	4.2
16	Floor Varnish	9.5
18	Floor Varnish	13.3
	Average	5.0

Five per cent shortage in measure represents a very fair profit to the manufacturer in itself.

588. **Significance of lime in varnishes.** The addition of five to six per cent of quicklime to melted rosin makes it considerably harder. The compound formed easily dissolves in linseed oil (at the present time wood oil is largely used), and when properly thinned forms the base of about all the cheap varnishes on the market. Such varnishes are characterized by giving a brilliant surface, easily scratched, and in a short time liable to crack badly. The relation between the percentage of lime (CaO) in the varnish and its toughness and elasticity is not marked enough to enable the chemist to pass judgment on its working qualities from the amount of lime it contains.

589. Sixteen of the leading varnishes on the market were tested out for toughness and elasticity, and then the amount of calcium oxide determined in each, the results obtained being given in the following table.

No.	Kind.	Per Cent of Calcium Oxide in Varnish.	Elasticity and Toughness.
2	Floor Varnish	0.868	Good
3	Floor Varnish	0.246	Good
4	Interior Varnish	0.200	Good
5	Exterior and Interior Varnish	0.178	Medium
6	No. 1 Coach Varnish	0.313	Good
7	Interior	0.195	Poor
9	Exterior	. . .	Medium
11	No. 1 Coach Varnish	0.265	Poor
13	Interior Varnish	0.271	Very Poor
14	Interior Varnish	0.161	Poor
15	Coach Varnish	0.800	Medium
17	Interior Varnish	0.158	Medium
19	Interior Varnish	0.158	Good
21	Interior Varnish	0.212	Good
23	Interior Coach Varnish	0.532	Poor
25	Interior Varnish	0.281	Poor

590. Of twelve brands of floor varnishes examined by the author, four were altogether too thin for the purpose intended; and of fourteen interior finishes, four were exceedingly thin, and several of the remainder were below average in this respect.

Of a total of twenty-six of the leading brands of floor, exterior and interior varnishes tested out by the author, seven were considered first class in all respects, eight were medium or just fair quality, while eleven were unquestionably poor and inferior both as regards working and the quality of the film after drying. Of the above eleven, eight were interior finishes.

591. The twenty-six with but two exceptions flashed at room temperature, a fact which is worthy of considerable attention on the part of the consuming public as regards fire risk.

CHAPTER XXXIII.

VARNISH STAINS AND COLOR VARNISHES.

592. Varnish Stains. Such data as may be obtained from an analysis of varnish stains is only of limited value as they are essentially varnishes carrying a small percentage of very finely ground colors, such as C. P. chrome green, sienna-red toner, etc. The moderate price at which these goods are offered, preclude the use of high-priced varnishes, and in order to obtain the desired effect usually a blend of two or more varnishes is used. Some of the most successful varnish stains are prepared by blending a straight China-wood-oil rosin varnish with a short-oil kauri-rosin (two-thirds low-priced kauri, one-third W. W. hardened rosin) varnish. Dark oak, light oak and walnut shades are obtained by adding sufficient asphaltum-rosin varnish to produce the desired effect; mahogany and rosewood by using a red toner in connection with the asphaltum black; light and deep cherry with raw sienna and red toner and the various greens with C. P. chrome green and small amounts of the asphaltum black.

These goods have been widely advertised during the last few years under various designations of which the word "lac" usually forms a part. The prevailing tendency has been to use inferior rosin varnishes which are not only brittle but scratch easily, showing the customary "rosin streak." A better class of goods can be prepared by adding a long-oil kauri or manila varnish to give elasticity.

593. Color Varnishes. The varnish stains, above described, possess two defects, they do not give clear, transparent effects owing to the fact that the pigments themselves are opaque. Also these pigments settle out on standing and more or less trouble is experienced in bringing them into uniform suspension when desired for use. These difficulties have been overcome by the use of colors soluble in the varnish such as the "fat colors," so called, and certain organic lakes. These afford a clean, transparent effect, and are easy to apply but they lack permanency of color. They are, however, widely used.

594. Stain Finishes. These finishes are designed to be applied over furniture or any interior finish, which has already been fully varnished, in order to give a mission, Flemish, Antwerp or similiar effect. In other words the stain, in a measure, sinks into the already applied varnish. These stains are prepared by dissolving various "fat colors," such as fat black, fat yellow, fat orange, fat red, fat brown, etc., in a combination of benzole, naphtha or petroleum spirits, and a long-oil varnish. These fat colors can be secured from any of the leading color supply houses and are aniline colors combined with a fatty acid, like oleic or stearic acid and sometimes rosin. While satisfactory to a certain extent, these finishes are not very durable, scratches showing badly because the color of the surface of the wood has not been changed.

595. Oil-wood Stains. This class of goods is very similiar to varnish stains, except that in this case the varnish is replaced by linseed oil. As found on the market they will contain 15 to 25 per cent of a light-colored boiled oil, and the balance naphtha or petroleum spirits, except for the small amount of pigment present.

The following analyses are characteristic of this class of goods.

	I. Green, per cent.	II. Cherry, per cent.	III. Dark Oak, per cent.
Linseed oil	14.0	16.4	18.0
Naphtha	79.0	77.4	75.0
Chrome green	7.0	.....	.....
Red toner	.....	6.2	.....
Asphaltum varnish	.....	.....	7.0[1]
	100.0	100.0	100.0

[1] Obtained by comparison.

Some manufacturers use a mixture of boiled and raw oil in order to regulate the drying. The separation of pigment and vehicle is best effected in a centrifuge.

CHAPTER XXXIV.

ENAMELS AND VARNISH SPECIALTIES.

596. Valuation. The essential consideration in the analyses of enamels, enamel finishes and varnish paints is the nature or composition of the vehicle which is largely varnish. The pigments that may be present in the above classes of products are of comparatively little moment as their analysis and duplication are exceedingly easy. The vehicle, on the other hand, offers many difficulties as it is usually prepared by the blending of two, three or even four varnishes of very diverse compositions and characteristics. The result being that the blend thus obtained behaves very differently as regards flowing, drying, toughness, hardness, etc., from the component varnishes. These variations in behavior often take unexpected directions, as for example, two varnishes each of which may be comparatively slow in drying, will, when mixed, dry quickly. It is, therefore, not possible for an analysis, even if exact, of a varnish to show anything of value as regards the physical or working qualities. It will, however, serve to give an approximate idea of the cost of the materials used, and at about what price the varnish in question could be duplicated. Having this information at hand, and a suitable variety of varnishes of known composition and properties to work with, it is not a difficult matter for an experienced chemist to very closely duplicate the various specialty products on the market. If the three requisite conditions above enumerated are not ob-

tained the value of any results that may be secured will be extremely uncertain.

597. Adoption of Analytical Methods. Recently considerable progress has been made in the valuation of varnish products by analysis and practically every varnish chemist has his own scheme which depends for its success very largely on intuition, judgment and the closeness with which he keeps in touch with the varnish industry. It is, therefore, difficult, if not impossible, to outline a scheme in print that can be followed and intelligent results obtained. The outline suggested by Dr. McIlhiney,[1] if worked over carefully by the chemist himself on varnish products of known composition, will establish certain relative standards which together with his own judgment and intuition will enable him to determine approximately the composition.

598. McIlhiney's Method. The oils and gums may be examined by McIlhiney's scheme as follows:

"The process, which is here described, depends upon the fact that although the union between oil and hard gum is too intimate to be broken up by the selective solvent action of any solvent acting directly upon the original mixture, the combination may be broken up and the oil and gum brought back to more nearly their condition, before they were melted together, by submitting the mixture to the action of caustic potash in alcoholic solution and subsequently acidifying the solution of potash salts so formed. By this means there is obtained from hard-gum varnishes a quantity of gum insoluble in petrolic ether very closely approximating the amount of hard gum actually existing in the varnishes, while the linseed oil is represented by its fatty acids which are readily soluble in this solvent unless

[1] Proceedings, Am. Soc. for Testing Materials, 1908.

they have been oxidized, in which case some of the fatty acids of the linseed oil will accompany the insoluble hard gum.

"In carrying out the method an opportunity is given to determine not only the weight of the oil and of gum, but also the Koettstorfer figure and the percentage of glycerin in the mixture. All these data taken together give a basis for corroborating the main figures.

599. "The process is carried out by weighing into an Erlenmeyer flask 2 to 10 grams of the varnish, adding a considerable excess of approximately half-normal solution of caustic soda or caustic potash in very strong or absolute alcohol, distilling off the major portion of the solvent, and redissolving in neutral absolute alcohol. The solution is then titrated with a solution of pure acetic acid in absolute alcohol, approximately half-normal strength, to determine the amount of the excess of alkali present. From this the Koettstorfer figure is determined as the exact strengths of the acid and alkali solutions have been ascertained independently by comparison with known standards. A further quantity of the standard solution of acid in alcohol is added so as to exactly neutralize the total amount of alkali originally added. By this means the acid bodies liberated from their combinations with alkali are obtained in solution in strong alcohol. To this solution there is now added a sufficient quantity of petrolic ether to dissolve the oil acids and this petrolic ether, being miscible with the strong alcohol, forms with it a homogeneous liquid. Water is now added to the mixture in such amount as to so dilute the alcohol contained that it is no longer a solvent for fatty or resin acids; this addition of water causes the petrolic ether which was mixed with the alcoholic liquid to separate, carrying with it the fatty acids.

The rosin goes with the fatty acids while the hard gum, being insoluble in either the petrolic ether or in the very dilute alcohol, separates in the solid state. The aqueous and ethereal layers are now separated in a separating funnel and each is washed, the watery layer with petrolic ether and the petrolic-ether layer with water. The petrolic-ether layer is now transferred to a weighed flask, the solvent distilled off and the residue of fatty acids and common rosin weighed. This latter is then examined further by Twitchell's method to determine the amount of rosin which it contains, or it may be examined qualitatively in a number of ways to establish its identity.

600. "The aqueous layer is freed from the suspended hard gum which it contains by filtering, and from any further quantity of gum which the weak alcohol may have retained in solution by evaporating off the alcohol and again filtering. The remaining aqueous liquid contains the glycerin and this is determined by the Hehner method with potassium bichromate — the method ordinarily used for examining spent soap lyes.

601. "The hard gum is according to this plan precipitated in such a way that it adheres to the sides of the glass vessel in which the alcohol and petrolic-ether mixture is diluted with water; the easiest method to weigh it is, therefore, to carry on the operation of dilution in a weighed glass vessel and then to dry and weigh the hard gum in this vessel. It frequently happens that some of the hard gum cannot be conveniently retained in this vessel but that it must be filtered out on a weighed filter and the weight so found added to that of the main portion.

602. "If the varnish contains non-volatile petroleum or other unsaponifiable matter it will naturally be in-

cluded in the fatty and resin acids, and it would be necessary to saponify the latter and extract the unsaponifiable matter from them while in the alkaline state; this operation is so familiar to chemists that it is mentioned here only to call attention to the necessity for it in some cases.

603. "It would naturally be expected that on account of the well-known insolubility of the oxidized fatty acids in petrolic ether, some of the acids of the linseed oil which had been polymerized by heat during the cooking of the varnish, or which had been oxidized during the blowing process to which some linseed oil is subjected before making it up into varnish, would fail to dissolve and would be counted in with the hard gum instead of with the linseed oil. It appears as a matter of fact that this source of error is of slight importance in the case of oil thickened by heat but that the blowing process gives an oil which is not completely accounted for by the soluble fatty acids recovered. This difficulty may be largely overcome by taking advantage of the greater solubility of the oxidized fatty acids in alcohol as compared with the hard gum; the freshly precipitated gum contaminated with oxidized fatty acids is treated with a moderate quantity of cold alcohol of about 85 per cent and allowed to digest for some time. The soluble matter so extracted is then recovered separately by evaporating off the alcohol.

604. "Rosin when present is usually combined with lime in the proportion of about 1 part of lime to 20 parts of rosin. An examination of the mineral constituents of the varnish is, therefore, of some value. The extraction of the mineral bases may be effected by treating a quantity of the varnish, somewhat thinned with benzine, with strong hydrochloric acid, and examining the aqueous liquid.

605. "The amount of fatty acids obtained represents about 92.5 per cent of the linseed oil. The identification of these fatty acids as belonging to linseed oil or to china wood oil may be satisfactorily accomplished in some cases, but there are undoubtedly many varnishes in which the analyst will be unable to identify and determine the oils. The odor and physical characteristics of the recovered gum are quite as important as the known chemical tests of which the acidity and the Koettstorfer figure are among the most important."

INDEX.

A.

PAGE

Acetic acid in white lead 99
Adulteration of turpentine 59
Aldehyde free alcohol 37
Agricultural paints 229
Aluminum silicate 86
Analysis of black pigments 185
Analysis of calcium carbonate pigments 82
Analysis of Chinese blue 206
Analysis of iron oxides 175
Analysis of leaded zincs 122
Analysis of petroleum thinners 75
Analysis of Prussian blue 204
Analysis of shellac varnish 255
Analysis of white lead 92
Analysis of white paints 143
Analysis of zinc pigments 107
Antimony vermilion 220
Asphaltum varnish 268

B.

Barium carbonate 79
Barium sulphate 77
Barn paint 237
Barrel paste 229
Borax 21
Bromine value of oils 44

C.

Calcium carbonate 80
Calcium sulphate 84
Carbon dioxide 97
Caustic soda 20
China wood oil 31
Chloride of lime 20
Chrome yellow 211
Classification of varnishes 275

PAGE
Cobalt blue 210
Cold-water paints 167
Combination emulsifiers 21
Composition of colored paints 170
Corn oil 28
Cottonseed oil 27
Covered testers 54
Crack and crevice fillers 234

D.

Damar varnish 255
Detection of water in paints 11
Dipping paints 232

E.

Enamels 282
Emulsions 17
Estimation of arsenic and antimony 117
Estimation of lead 111
Estimation of mineral oil 25
Estimation of petroleum products 52
Estimation of rosin oil 45
Estimation of water 12, 14
Estimation of wood alcohol 250
Excessive use of volatile oils 57
Evaporation test 46

F.

Fineness of pigments 124
Fire test 56
Fish oil 28
Flash point 38
Flat wall finishes 138
Free fatty acids 36
Functions of turpentine 32

G.

Geer's modification 67
Gravity of pigments 127

H.

Heavy turpentine 68
Hexabromide test 47

I.

	Page
Inert pigments	77
Iodine number	32
Iodine number of oils	35
Iron fillers	234

J.

Japans and driers	239

K.

Kalsomine	163
Koettstorfer number	36

L.

Labeling paint products	1
Lakes	165
Linseed oil constants	32
Linseed oil foots	41
Linseed oil specifications	47
Litharge	222
Lithopone	122
Long oil varnish	262

M.

Magnesium silicate	86
Metallic lead	94

O.

Oil from inferior seed	39
Oil reductions	137
Oil varnishes	257
Oleate of lead	19
Orange mineral	221
Open testers	56

P.

Paris white	80
Paste wood filler	91
Petroleum thinners	72
Practical testing of varnish	269
Practical testing of paint	129
Priming enamels	229
Priming ochres	182
Prussian blue	204

R.

PAGE
Ratio of pigment to vehicle 10
Red lead 221
Rosin oil 29
Rough stuff 234

S.

Sandy lead 93
Saponification value 36
Separation of mineral oil 26
Separation of vehicle 5
Separation of volatile oils 23
Shade cloth paint 229
Shellac 245
Shellac varnish 247
Shingle stain 236
Short oil varnish 261
Silica 87
Soya-bean oil 30
Specific gravity 24
Spot test 24

T.

Thermometer correction 139
Tinting strength 126
Turpentine 19, 59, 60, 62
Turpentine reductions 138
Typical analysis of mixed paints 157

U.

Uniform sample 4
Use of centrifuge 6

V.

Varnish stains 279
Vermilion 211
Vermilion primer 229

W.

Whiting 80
Wood fillers 223
Wood turpentine 63, 64, 67

Zinc sulphate 110
Zinc white 116